Recent Advances in Design of Electrocatalysts for High-CURRENT-DENSITY Water Splitting

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Electrochemical water splitting technology for producing “green hydrogen” is important for the global mission of carbon neutrality. Electrocatalysts with decent performance at high current densities play a central role in the industrial implementation of this technology. This field has advanced immensely in recent years, as witnessed by many types of catalysts designed and synthesized toward industriallyrelevant current densities (>200 mA cm²). By discussing recent advances in this field, several key aspects are summarized that affect the catalytic performance for high-current-density electrocatalysis, including dimensionality of catalysts, surface chemistry, electron transport path, morphology, and catalyst-electrolyte interplay. The multiscale design strategy that considers these aspects comprehensively for developing high-current-density electrocatalysts are highlighted. The perspectives on the future directions in this emerging field are also put forward.

1. Introduction

Energy, water, and the environment are three of the top ten challenges faced by human beings now and in the next tens of years, as proposed by the late Nobel laureate Richard E. Smalley.[1] According to the International Energy Agency, world energy consumption had grown to 9938 Mtoe (million tons of oil equivalent) in 2018, of which about 70% was from fossil fuels, resulting in a record high CO₂ emission of over 33 gigatons.[2] The need to address the problems of environment and climate changes is driving a dramatic global revolution of energy systems. The electricity accounts for nearly 20% of the world’s total energy consumption nowadays,[2] which is expected to overtake oil and coal and reach >30% in 2040.[3] The growing demand for renewable energy is a main driving force behind the rising electricity use, in which two-thirds of it is expected to be generated from renewable resources in 2040,[4] with a projected electricity price of less than 10 US cents per MWh by 2050.[4]

The need for renewable energy integrated with electricity generating systems is becoming more urgent than ever,[5] which requires the development of advanced energy conversion and storage technologies.[6] A sustainable way is to produce “green hydrogen” by electrochemical water splitting,[7,8] coupled with electricity produced from renewable resources, as shown in Figure 1. Hydrogen is not only a promising alternative energy carrier to fossil fuels,[9] but also a crucial feedstock in industry for fertilizer production, petroleum refining, and hydrogenation.[10] The main reactions involved in electrochemical water splitting include the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In the context of global carbon neutrality, the importance of “green hydrogen” by electrochemical water splitting technology has attracted massive attention not only by the scientific community but also by governments and industries around the world.

For industrial use, developing electrocatalysts with a good performance under the industriallyrelevant conditions including high current density (HCD), long working time, and demanded pressure and temperature, is crucial. The industriallyrelevant current density is necessary because HCD means demanded pressure and temperature, is crucial. The industriallyrelevant current density is necessary because HCD means a high rate of hydrogen production, which can reduce capital expenditures and lead to a profitable hydrogen production. In this regard, many governments and organizations have proposed different technical targets for HCD water splitting which are needed for different applications. For example, the current density requirement for the central proton exchange membrane (PEM) water electrolysis is 1500 mA cm² at cell voltage of 1.75 V in 2015 and will reach 1600 mA cm² at 1.66 V in 2040, according to technical targets from the U.S. Department of Energy (DOE).[10] The Fuel Cells and Hydrogen Joint Undertaking in Europe (FC HJU) proposes more ambiguous goals showing that a current density of 800 mA cm² for alkaline water electrolysis and 2500 mA cm² for PEM water electrolysis should be achieved in 2030. Table 1 summarizes some future targets of performance metrics of water splitting technologies. These targets motivate studies of electrochemical water splitting under HCD conditions.

Electrocatalysts with high performance play a central role in electrochemical water splitting to reduce electricity consumption and they are essential to reach these performance targets. In the past several decades, substantial progress in the development of low-dimensional electrocatalysts has been...
made, especially in exploring active sites and developing new catalysts.[12–18] These catalysts, however, are commonly studied under laboratory conditions (e.g., with current density of $1^{-100} \text{ mA cm}^{-2}$) and research related to the water splitting is mainly focused on fundamental catalytic kinetics.[19] The optimization of a single physical property such as the Gibbs free energy of adsorption for intermediates at a low current density does not usually result in a good HCD performance because the activity and stability of catalysts are also affected by local reaction environment, which is closely related to current density. This fact indicates a large gap between current electrocatalyst studies that focus on low current density conditions and the practical applications where HCD is needed. The research of HCD electrocatalysts is an important aspect in the field of water splitting as it is closely related to the practical applications of this technology. In the past few years, an increasing number of catalysts have been designed and tested, but only few of them deal with industriallyrelevant current densities. For example, there are more than 1200 papers in 2014 with the topic of water electrolysis, among them only about 40 papers refer to HCD water electrolysis (Figure 2). Although there are increasing numbers of papers on the development of HCD catalysts, it is still in their infancy as only less than 5% of papers are related to HCDs in all the papers about water electrolysis. Clearly, more efforts should be devoted in HCD considering its importance to the large-scale practical implementation of electrolysis.

The state-of-the-art electrocatalysts developed for HCD water splitting include HER electrocatalysts such as Pt-based nanoparticles,[20,21] transitional metal phosphides,[22,23] sulphides,[24,25] and oxides,[26] as well as OER electrocatalysts such as Ir- and Ru-based nanoparticles,[21,27,28] transitional metal (oxy)hydroxides,[29–31] and other derived catalysts[32,33] (Table 2). Catalysts containing low amounts of noble metals or non-noble metal catalysts are highly desired to reduce the cost of water splitting. Although most of these catalysts are tested in a batch-type cell, some of them have been tested in ion exchange membrane-based electrolyzers. In PEM electrolyzers, non-noble metal phosphides have shown HER performance almost comparable to commercial Pt/C catalysts.[22] For OER, however,

**Table 1. Summary of the performance targets for high-current-density water electrolysis technologies.**

| Source | Technology | Current density [mA cm$^{-2}$] | Voltage [V] | Energy efficiency [%] | Stability | Temperature [°C] | Pressure [atm] |
|--------|------------|-------------------------------|-------------|------------------------|-----------|-----------------|---------------|
| U.S. Department of Energy[10] | Proton exchange membrane electrolysis | 1600 (in the year 2040) | 1.66 | 74 | 50 000 h | 50–85 | 68 |
| Fuel Cells and Hydrogen Joint Undertaking in Europe[11] | Proton exchange membrane electrolysis | 2500 (in the year 2030) | n/a | n/a | Degradation by 0.12% per 1000 h | n/a | n/a |
| Fuel Cells and Hydrogen Joint Undertaking in Europe[11] | Alkaline water electrolysis | 800 (in the year 2030) | n/a | n/a | Degradation by 0.1% per 1000 h | n/a | n/a |
### Table 2. Summary of state-of-the-art electrocatalysts for high-current-density water splitting.

| Reaction | Catalyst | Performance | Testing conditions | Ref. |
|----------|----------|-------------|-------------------|------|
| HER | Fe doped Ni$_3$P in CNT | 183 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on nickel foam, electrode area: $\approx$1 cm$^2$ | [37] |
| | Ni-W nanosheet | 303 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on glassy carbon, electrode area: 0.2475 cm$^2$ | [38] |
| | Ni$_2$Mo$_3$N/Ni | 70 mV @ 300 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [39] |
| | Pt-Ni-Mo | 42 mV @ 2000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [20] |
| | Ni$_2$P/NF | 306 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [40] |
| | MoC$_6$/MoS$_2$ | 220 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ti foil, electrode area: $\approx$1 cm$^2$ | [24] |
| | Ni-NiMoFe | 97 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: 1 cm$^2$ | [41] |
| | GDI/MoO$_3$ | 1850 mV @ 1200 mA cm$^{-2}$ | Batch-type cell, 0.1 M KOH, on Cu foam, electrode area: 1 cm$^2$ | [26] |
| | CoP HNS/CF | 180 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, on carbon foam, electrode area: $\approx$1 cm$^2$ | [42] |
| | 2H-Nb$_{13}$S$_2$ | 420 mV @ 5000 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, on glassy carbon, electrode area: not referred to | [25] |
| | Ta-TaS$_2$ | 398 mV @ 2000 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, material itself as both electrodes and catalyst, electrode area: $\approx$1 cm$^2$ | [43] |
| | MoC$_6$/MoS$_2$ | 227 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, on Ti foil, electrode area: $\approx$1 cm$^2$ | [24] |
| | α-MoB$_2$ | 334 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, on Cu foil, electrode area: $\approx$1 cm$^2$ | [44] |
| | Pt/Ca | 113 mV @ 600 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, material itself acts as both electrode and catalyst, electrode area: not referred to | [21] |
| | HC-MoS$_2$/Mo$_3$C | 414 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, on Cu foam, electrode area: $\approx$1 cm$^2$ | [45] |
| | Ta-TaS$_2$ (HER) || IrO$_2$ | 1.98 V @ 1000 mA cm$^{-2}$ | PEM electrolyzer, ambient condition, electrode area: 1 cm$^2$ | [43] |
| | CoP (HER) || IrO$_2$ | 2.02 V @ 1860 mA cm$^{-2}$ | PEM electrolyzer, at 55 °C, 400 psi, electrode area: 86 cm$^2$ | [22] |
| | Pd/PG (HER) || RuO$_2$ | 2.32 V @ 2000 mA cm$^{-2}$ | PEM electrolyzer, at 80 °C, catalyst on PEM, electrode area: 25 cm$^2$ | [46] |
| | MoS$_2$/N/NCNT (HER) || IrO$_2$ | 2.36 V @ 4000 mA cm$^{-2}$ | PEM electrolyzer, at 80 °C, on carbon cloth, electrode area: 5 cm$^2$ | [47] |
| | MoP/C-B (HER) || Ir/C | 1.81 V @ 500 mA cm$^{-2}$ | PEM electrolyzer, at 80 °C, on carbon paper, electrode area: 5 cm$^2$ | [23] |
| | NiCu mixed metal oxide (HER) || Ir/C | 2.0 V @ 1850 mA cm$^{-2}$ | PEM electrolyzer, at 50 °C, on carbon paper, electrode area: 25 cm$^2$ | [48] |
| | MoS$_2$/Mo$_3$C | 300 mV @ 860 mA cm$^{-2}$ | Batch-type cell, 0.1 M KOH, on Pt microelectrode, electrode area: $\approx$100 µm$^2$ | [32] |
| | Co doped FeNi carbonate hydride | 254 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 0.5 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [29] |
| | Nanostructured NiFe (oxy)hydroxide | 261 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [30] |
| | Ni–Fe oxyhydroxide @ NiFe alloy | 248 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [31] |
| | Ni–Fe MOFs | 258 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [31] |
| | Fe$_2$(PO$_3$)$_3$/Ni$_3$P | 265 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Pt microelectrode, electrode area: $\approx$100 µm$^2$ | [33] |
| | Co$_3$Mo$_2$/Cu | 390 mV @ 400 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, material itself acts as both electrode and catalyst, electrode area: $\approx$1 cm$^2$ | [49] |
| | VOs-Co$_3$O$_4$/CoO NWs@Cu@NF | 391 mV @ 1000 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [50] |
| | Ni$_8$Fe$_2$–ONCs | 255 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [51] |
| | a–c–FeOOH | 330 mV @ 300 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [52] |
| | Fe$_3$P/Ni$_3$P | 280 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [53] |
| | Se doped FeOOH | 348 mV @ 500 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on Ni foam, electrode area: $\approx$1 cm$^2$ | [54] |
| | NiCo-r | 320 mV @ 285 mA cm$^{-2}$ | Batch-type cell, 1 M KOH, on glassy carbon, electrode area: $\approx$0.07 cm$^2$ | [55] |
| | W–Ir–B alloy | 497 mV @ 2000 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, material itself as both electrodes and catalyst, electrode area: $\approx$0.314 cm$^2$ | [56] |
| | H-Ti@IrO$_2$ | 336 mV @ 200 mA cm$^{-2}$ | Batch-type cell, 0.5 M H$_2$SO$_4$, on a large surface-area Ti foam, electrode area: 1 cm$^2$ | [57] |
| | Pt/C || RuO$_2$/SnO$_2$ (OER) | 1.72 V @ 1000 mA cm$^{-2}$ | PEM electrolyzer, at 80 °C, catalyst on PEM, electrode area: 4 cm$^2$ | [27] |
| | Pt/C || Ir$_6$Ru$_4$O$_2$ (OER) | 1.57 V @ 1000 mA cm$^{-2}$ | PEM electrolyzer, at 80 °C, catalyst on PEM, electrode area: 5 cm$^2$ | [28] |
the activity and stability of non-noble metal catalysts still need to be improved.\[34\] Moreover, in anion exchange membrane (AEM) electrolyzers, non-noble metal catalysts are stable and available, thus efficient AEM catalysts are worthy of extensive studies.\[35,36\] It is clear that great efforts need to be devoted to exploring high-performance and cost-efficient electrocatalysts for the HCD water splitting.

In the light of recent progress in HCD electrocatalysts, this Review first summarizes the progress in design of HCD electrocatalysts. The catalysts discussed here are those commonly tested at a current density larger than 200 mA cm$^{-2}$ unless pointed out otherwise. Such a threshold current density is chosen because the operation current density is usually higher than it in industry.\[24\] Several key aspects that determine the HCD performance of catalysts are discussed, including catalyst dimensionality, surface chemistry, structures, electron transport path, and catalyst-electrolyte interplay, followed by a discussion of the advances and opportunities in the multiscale design of HCD catalysts. Finally, we propose several future directions for research in this important field. This Review mainly focuses on HCD electrocatalysts. Design of devices and systems as well as economic analysis on water electrolysis have been well reviewed\[60\] and are not discussed in detail in this Review.

### 2. Effect of Current Density on Catalytic Performance

Catalytic performance is sensitive to local reaction environment, which is affected by current density. Basically, there are two main differences between high and low current density conditions. First, HCD usually means that a large bias is applied to catalysts, leading to an extreme polarization condition far from the equilibrium potential. Second, the electrochemical reaction is violent and fast under HCD conditions, accompanied by the fast consumption of reactants and fast generation of products near the catalyst surface. These differences cause catalytic performance at HCDs different to that at low current densities. The overpotential ($\eta$) of reactions as well as the stability are two main performance metrics, which reflect the effect of HCDs on water splitting. For easier understanding, effect of the HCDs on catalytic performance is compared with low current densities and is discussed from two perspectives of electron transfer and mass transfer (Figure 3). Next, we will show recent progress in understanding how the current density acts on catalytic performance, as the basis of designing electrocatalysts for HCD water splitting.

First, current density affects electron transfer process of reaction that happens at catalyst-electrolyte and catalyst-support interfaces. The performance of catalysts is shown by overpotentials for those tested in a batch-type cell and full cell voltages for those tested in a PEM or an AEM electrolyzer. MOFs stand for metal-organic frameworks; CNTs stand for carbon nanotubes; PEM stands for proton exchange membrane; AEM stands for anion exchange membrane.

![Figure 3](image-url)

**Figure 3.** Physical models of the electron and mass transfer processes under HCD conditions. Schematics show a) electron transfer and b) mass transfer processes at HCDs. Here, support denotes all the materials to load catalytic materials and delivery electrons, and catalyst denotes the catalytically active material or component for reactions.
interfaces (Figure 3a). At the former interface, catalytic activity is largely determined by the energy needed for adsorption/desorption of intermediates and the rupture/formation of chemical bonds. Recent works show that current densities can affect electron-transfer overpotentials by changing the activity of catalysts, such as Pt, IrO$_2$, MoB, and Fe-NiOOH. For example, Nong et al. find that the current density acts on the catalytic activity by accumulating charges in the catalysts. In this work, oxidative charges are accumulated and the surface total hole coverage increases with the applied voltage, which are coupled with the electron transfer from IrO$_2$. As a result, the activation free energy for bond formation and rupture decreases linearly with the applied voltage, showing a Tafel slope reducing from 77 to 39 mV dec$^{-1}$ at a voltage up to 1.58 V, resulting, the activation free energy for bond formation and rupture decreases linearly with the applied voltage, showing a Tafel slope reducing from 77 to 39 mV dec$^{-1}$ at a voltage up to 1.58 V, and a higher OER activity at relatively high current densities. This correlation between current density and catalytic activity is also shown in MoB and Pt catalysts for HER. For example, Chen et al. find that MoB catalyst shows a unduly negative performance under HCD conditions. All in all, the current density affects electron transfer process happened at the catalyst-electrolyte and catalyst-support interfaces.

Second, current density affects mass transfer process of reaction that happens at the gas-liquid-solid interface containing reactant, product, and catalyst (Figure 3b). The fast consumption of reactants near the catalyst under HCDs may decrease its catalytic performance. Liu et al. show that concentration of OH$^-$ reactant around the tips of Ni$_x$Fe$_{1-x}$ nanoarrays is high even at HCDs, delivering a current density of 500 mA cm$^{-2}$ at 255 mV for OER in 1.0 m KOH. It should be noted that the formation rate of H$_2$ or O$_2$ bubbles dramatically increases at HCD water splitting and thus hinders reaction process. As shown by some works, thickness of bubble layers increases with the current density and bubbles adhered to catalyst surface cover most of catalyst surfaces and deteriorate their catalytic performance under HCD conditions. Lu et al. synthesize MoS$_2$ catalysts with flat and nanostructured morphologies. The latter one shows a superaerophobic nature and thus the sizes of adhesive bubbles are much smaller than those on the flat MoS$_2$, resulting in a low overpotential of 500 mV at 170 mA cm$^{-2}$. These works show that current density plays a great impact on mass transfer process and bubble removal on catalysts.

Third, the stability of catalysts, mechanically or chemically, is also influenced by current density. On the one hand, because bubbles adhered on catalyst exert a strong interfacial adhesion force on catalyst when they depart from the catalyst, some parts of the catalyst may peel off by the bubbles and deteriorates mechanical stability of catalyst. Such a peeling-off issue of catalyst usually becomes serious as current density increases unless the interaction force between the catalyst and support is stronger than interfacial adhesion force between the catalyst and bubble. As demonstrated by some binder-free catalysts, they show superior stability under HCD conditions. For example, Zhang et al. report a catalyst composed of CoOOH encapsulated Ni$_3$P tubular arrays, which shows a stability over 100 h at 1200 mA cm$^{-2}$ for HER. They show that such a catalyst buffers the shock of electrolyte convection and hydrogen bubble rupture through release of stress. Despite the progress, the threshold value of interaction force between catalyst and support over which the catalyst will show good robustness under HCDs still needs to be found. On the other hand, HCD may lead to a challenge in chemical stability of catalysts. It is an even serious issue for OER catalyst because the catalyst suffers from a strong oxidation potential at high current densities, which usually results in oxidation or reconstruction of catalyst and the reconstructed structure may be unstable in electrolytes. Qin et al. study the chemical stability of Co$_x$M$_{3-x}$O under HCDs and find that incorporation of Ni in the spinel Co$_3$O$_4$ improves its long-term chemical stability, while doping of Mn and Ge to spinel Co$_3$O$_4$ has an opposite effect. As a result, Co$_x$Ni$_{3-x}$O$_4$ shows the stability over 140 h at 1000 mA cm$^{-2}$ in 1 m KOH for OER. In contrast, other catalysts only run for less than 40 h under the identical conditions. In sum, the effect of current density on mechanical and chemical stability of catalysts should be considered.

Apart from the aforementioned similarity effects that current density acts on catalyst performance, differences between
OER and HER under HCD conditions are also noteworthy. First, OER catalyst suffers an oxidation potential at which most metals and compounds are oxidized and reconstructed, leading to the change in activity and stability of catalysts. Such a change becomes critical to designing OER catalyst at HCDs. Second, the diffusion coefficient of OH$^-$ ($5.273 \times 10^{-5}$ cm$^2$ s$^{-1}$) for OER is smaller than that of H$^+$ ($9.311 \times 10^{-3}$ cm$^2$ s$^{-1}$) for HER, thus mass transport efficiency for OER would be more challenging than HER at HCDs. Third, the pH value affects HCD performance of catalysts. State-of-the-art HER catalysts usually work well in acidic electrolytes while OER catalysts in alkaline electrolytes. Fourth, the local environment near the surface of OER catalysts tends to be more acidic than bulk electrolyte in a PEM electrolyzer and more alkaline in an AEM electrolyzer, making the stability request of OER catalyst crucial. Altogether, the effects of the current density on HER and OER catalysts are different in several aspects.

3. Key Aspects Need to be considered for Designing HCD Catalysts

Then, we will introduce the recent progress in design of electrocatalysts for HCD water splitting. Five key aspects that are used to engineer catalyst performance at HCDs are summarized and discussed, including catalyst dimensionality, surface chemistry, morphology, electron transport path, and catalyst-electrolyte interplay (Figure 4). Note that some factors that do not affect the performance of catalysts greatly at low current densities become important under HCD conditions. Because some of the factors are also used to engineer the catalyst activity at low current densities, we will focus on the differences of HCDs and avoid discussion about the overlap parts between high and low current densities.

3.1. Catalyst Dimensionality

We shall refer to electrocatalyst particles such as 0D single atoms and nanoparticles, 1D nanowires and nanotubes, and 2D nanosheets, as “low-dimensional”. The low dimensionality has been reported as an efficient strategy to engineer the HCD performance of catalysts. Electrocatalysts with low dimensionality show many unique points over the bulk catalysts. For example, these materials usually have high specific surface areas, short paths for electron transport in certain directions, variable chemical/physical properties, and the ability to assemble into 3D hierarchical structures. In addition, they show unique properties stem from the dimension effects. 0D nanoparticles can be easily assembled on gas diffusion layers and ion exchange membranes into thin films with large size and good uniformity. Besides nanoparticles, other nanomaterials such as single atom, 1D, and 2D catalysts also show their advantages. It is known that single atom catalysts have the highest efficiency of atoms and mass activity for catalysis. Moreover, they have a high stability by forming strong chemical bonds with the support materials. 1D catalysts such as carbon nanotubes have curved surfaces that can improve the reaction selectivity. 2D catalysts such as MoS$_2$ can work as model catalysts for mechanism studies because they are atomically flat and have precise structures. Interestingly, they can also be produced from the corresponding bulk materials by top-down methods making the scaling-up production of 2D catalysts feasible. These properties of low-dimensional catalysts may influence their performance at HCDs by changing the electron transfer and mass transfer processes and thus engineering the dimensionality of catalysts has been used as a strategy of changing catalytic performance at HCDs.

The catalytic performance for HCD water splitting is improved by enhancing electron transfer processes with low dimensionality of catalysts, as shown in Figure 5a. The surface electronic structure of the catalyst and number of coordinated unsaturated atoms in it can be readily engineered by the catalyst particle size, strain, defect, and the ligand effect. Detailly, i) the low-dimensional catalysts would show fast electron transfer at the catalyst-electrolyte interface and result in a better catalytic activity than bulk materials, and this method uses a consistent idea of increasing catalytic activity at low current densities. ii) Taking use of low dimensionality to offer a number of active sites that are exposed to reactants, so that the reaction rate increases per electrode area and the HCDs are achieved at a relatively small overpotential. For instance, Bao et al. show that NiCo$_2$O$_4$ ultrathin nanosheets rich in oxygen-vacancy active sites exhibit a current density of 285 mA cm$^{-2}$ at an overpotential of 320 mV, which is superior to the corresponding bulk catalyst and samples with few active sites. iii) Researchers also find that the low dimensionality of catalysts leads to fast electron transfer at the interface by inducing a spatially inhomogeneous electric field in catalysts, which causes an even strong potential bias at any sharp points on them. iv) Low-dimensional catalysts may have short paths for electron transport or small resistances at the catalyst-support interfaces so as to decrease electron transfer overpotential at HCDs. For instance, Liu et al. show catalytically active Co$_{3}$O$_{4}$/CoO nanowires that are in situ grown on Cu nanopillars. Such a catalyst shows a relatively lower electron transfer resistance than other control samples, and delivers a current density of 1000 mA cm$^{-2}$ at an overpotential of 391 mV. Altogether, the electron transfer processes at interfaces and inside catalysts are usually greater in low-dimensional catalysts, which guarantee the good catalytic performance for HCD water splitting.

The catalytic performance for HCD water splitting is also improved by enhancing mass transfer processes of low-dimensional catalysts, as shown in Figure 5b. i) The low-dimensional catalysts may induce a changed concentration of reagents/reactants on catalyst, which changes the local chemical potential and improves the catalytic performance at HCDs. For example, Liu et al. design a Ni$_x$Fe$_{1-x}$ nanocone array catalyst and compare its catalytic performance at HCDs with those having different tip curvature radii. Their results show that the one with the sharpest tip can concentrate the reactants near the tip and boost its OER performance at HCDs. ii) Low-dimensional catalyst is efficient to remove H$_2$ and O$_2$ bubbles when it is small enough because it can reduce the lengths of contact lines at gas-liquid-solid interfaces and thus reduce the interfacial adhesion force between catalysts and bubbles, which benefits catalytic performance at HCDs. For instance, by engineering MoS$_2$ into flat, micro-structured, and nano-structured films, Lu et al. show that
the nanostructured one shows the highest HER performance at a current density up to 100 mA cm\(^{-2}\).[75] On the nanostructured MoS\(_2\), H\(_2\) bubbles generate and left the catalyst quickly before they grow up to 100 µm in diameter, while bubbles do not leave the flat catalyst unless their diameters are larger than 400 µm. The large numbers of coordinated unsaturated atoms on the surface and the different surface electronic states of low-dimensional catalysts influence their interactions with reactants or products by the electrostatic interaction, van der Waals interaction, hydrogen bonding, etc. Such effects directly influence the interfacial adhesion force and thus the mass transfer process. In addition, the mechanical stability of the catalyst related to the removal of bubbles can be improved. The interfacial adhesion force \(F_{\text{int}}\) increases with the bubble radius \(r\) and may be larger than the adhesion force of a catalyst film on the support \(F_{\text{ad}}\) and therefore rupture the catalyst \(F_{\text{int}} > F_{\text{ad}}\), unless gas-liquid-solid interfaces \(L(r)\) remain small at HCDs. Specifically, a small bubble with a surface tension \(\sigma\) of \(\approx 10\) N mm\(^{-1}\) generates a small interfacial adhesion force \(F_{\text{int}} = \sigma \times L\) of \(\approx 10^6\) N when \(L\) is only 0.1 mm, which is smaller than electroplated catalyst films with the \(F_{\text{ad}}\) of \(\approx 10^6-10^7\) N (if \(r = 0.1\) mm).[92] Therefore, the low dimensionality of catalysts has been used to enhance not...
only the mass transfer efficiency of catalysts but also their mass transfer process-related mechanical stability.

3.2. Surface Chemistry

Engineering surface chemistry of catalysts can tune catalyst performance for HCD water splitting by 1) changing the bond strength between intermediates and catalytic sites and 2) improving the mass transfer efficiency of catalysts (Figure 6a). Indeed, catalyst surface (e.g., composition, structure, defect, strain, doping), heterostructure with interfacial interaction, and surface spectator, etc., all influence the surface chemistry of the catalysts and some of them have been used to tune HCD performance.\[93–97\] Engineering the surface chemistry of catalysts is a basis to achieve high performance at HCDs.

Engineering catalyst surface changes the surface electronic structure and the bond strength between intermediates and active sites. For example, Luo et al. design a catalyst that composes of the MoS2 nanosheets with Mo2C nanoparticles decorated on their edges (MoS2/Mo2C), which shows a superior performance at HCDs as compared with the pure MoS2 catalyst (Figure 7a).\[24\] Specifically, it shows overpotentials of 227 mV in acidic medium and 220 mV in alkaline medium at the current density of 1000 mA cm\(^{-2}\). Although MoS2 and MoS2/Mo2C catalysts show the same microscopic morphology, they have different surface chemistry compositions (Figure 7b). The latter one shows fast HER kinetic due to surface oxygen groups formed on Mo2C during the HER process, which decreases the energy barriers for both adsorption/desorption of hydrogen and dissociation of water at HCDs. Moreover, they find that such a difference in surface chemistry makes the bubble release easily on Mo2C/Mo2C catalyst and fast mass transfer efficiency. In another example, Zheng et al. design a MoS2 nanofoam catalyst co-confining selenium in the surface and cobalt in inner layers (Figure 7c,d).\[98\] By engineering the surface chemistry of MoS2, the catalyst needs an overpotential of 382 mV to deliver a current density of 1000 mA cm\(^{-2}\) (Figure 7e) and its performance is stable for 360 h without decay. The theoretical results attribute the HCD performance to the optimized hydrogen adsorption activity of both in-plane and edge active sites on the doped MoS2. Recently, single atom catalysts loaded on proper supports are also used for HCD water splitting due to their advantages of high atom utilization efficiency and high activity.\[99,100\] For example, Liu et al. show that by loading 0.49 wt% Pt single atoms on RuCeO\(_x\), the catalyst shows an overpotential of 320 mV at 600 mA cm\(^{-2}\) and is better than commercial 20 wt% Pt/C catalyst.\[101\]

Constructing heterostructures with charge transfer through the interfaces of each component is another strategy to tune catalyst performance at HCDs. For example, Yao et al. report that a graphdiyne/molybdenum oxide (GDY/MoO\(_3\)) catalyst shows a sp C–O–Mo hybridization on the interface between graphdiyne and molybdenum oxide (Figure 7f,g), which facilitates the charge transfer and boosts the dissociation process of H\(_2\)O molecule.\[86\] The heterostructure exhibits a current density of 1200 mA cm\(^{-2}\) at an overpotential of about 1850 mV in 0.1 m KOH, which exceeds both the HER performance of graphdiyne and molybdenum oxide catalysts without such an interfacial interaction (Figure 7h).

In addition to the surface composition of the catalyst and heterostructure structure, surface spectators that are chemically bonded to or form a composite/heterostructure with the catalyst also affect HCD performance. Surface spectator referred herein is a type of specie that may adhesive to or bonding to the catalyst surface. It affects the stability of intermediates and the reaction process while itself may not be catalytic site. Their functions include, but are not limited to, the destabilization of reactant species, and changing the bond strength between intermediates and catalytic sites.\[102\] despite that the spectators may be not catalytic sites in the catalytic materials. All the progress shows that surface chemistry engineering is an effective strategy for designing catalysts for HCD water splitting.

It is noted that OER catalysts usually show much slower reaction kinetics than HER catalysts and designing OER catalysts at HCDs by surface chemistry strategies toward high activity is worthy of more discussion. The crystalline phase and amorphous phase are used to design active catalysts for OER at HCDs.\[52,103\] For example, Qiu et al. show a FeOOH catalyst with rich amorphous-crystalline phase boundaries that delivers 300 mA cm\(^{-2}\) at an overpotential of 330 mV, surpassing OER activity of either the amorphous phase or the crystalline phase FeOOH. Besides phase engineering, the control of self-reconstruction of OER catalysts is recently reported.\[35\] Wu et al. find that a low level of Fe substitution can facilitate the surface...
reconstruction of CoAl₂O₄ catalyst and Al³⁺ leaching, which finally leads to the self-termination of catalyst. Such a CoAl₂O₄ catalyst is tested in an AEM electrolyzer using Pt/C HER catalyst, delivering 1000 mA cm⁻² at a cell voltage of about 1.96 V at 60°C in 0.1 M KOH. [35] In sum, some strategies of engineering surface chemistry of OER catalysts at HCDs have been developed that need further exploration.

3.3. Nano, Micro, and Macroscale Structure of Catalyst

Because the catalyst is used in the form of a film that has to contact a current collector (or support), each unit of low-dimensional catalysts (the building blocks of the film) need to be assembled in a certain way. The nano, micro, and macroscale structure of such a catalyst film jointly determine the
size of the channels and the exposure of active sites to the electrolyte (Figure 6b). This is also an aspect that can be engineered toward better HCD performance for water splitting by 1) increasing mass transfer ability and 2) increasing the numbers of active sites for catalysis. Note that the effect of the sizes of the building blocks on HCD performance has been discussed in the part 3.1 "catalyst dimensionality".

First, the channels (pores) constructed by catalytic building blocks are engineered to ensure smooth electrolyte supply and bubble removal, and thus decreasing the mass transfer overpotential for HCD water splitting.[104–106] For example, Park et al. show that the CuCo-oxide OER catalyst grown on a nickel foam delivers a current density of 2200 mA cm$^{-2}$ at a cell voltage of 1.9 V using Pt/C as HER catalyst (Figure 8a).[58] They use their catalyst in an anion exchange membrane water electrolyzer and compare the mass transfer overpotential with the IrO$_2$ catalyst. At a current density larger than 200 mA cm$^{-2}$, the mass transfer overpotential contributes greatly to the total overpotential, which accounts for 10.4% on CuCo-oxide catalyst while 35.4% on IrO$_2$ catalyst at 1200 mA cm$^{-2}$ (Figure 8b). The CuCo-oxide catalyst shows a much smaller mass transfer overpotential due to its highly porous structure constructed by catalytic building blocks that ensure smooth supply of electrolyte at HCDs (Figure 8c). Yu et al. report a catalyst film consisting of Ni$_2$P nanowire arrays grown on a Ni foam (Figure 8d–f), which enables the fast release of H$_2$ bubbles in the HER at HCDs and delivers 1000 mA cm$^{-2}$ at an overpotential of 306 mV (Figure 8g).[40] Despite decade of efforts, more quantitative understanding of the effects of channel or pore sizes on mass transfer and catalyst performance is still needed.

Second, the exposure of catalytic sites to the electrolyte ensures efficient uses of the catalyst and enables the availability of many active sites, with which catalyst performance at HCDs increases. For example, King et al. report a catalyst composed
of CoP nanoparticles on the surface of a high-surface-area carbon support that is integrated into an 86 cm² PEM electrolyser (Figure 9h,i). Despite its lower mass activity than the commercial Pt nanoparticles, it shows a good apparent current density due to the large loading of CoP, which operates at 1860 mA cm⁻² for >1700 h (at 50 °C and 400 psi, pounds per square inch) of continuous hydrogen production (Figure 8j). Engineering the exposure of catalytic sites on conductive supports to electrolyte is a common strategy that has been widely used. The role of nano, micro, macroscale structures of the catalyst on the HCD electrocatalysis involves controllable assembly of low-dimensional building blocks into hierarchical catalyst that needs more study. To date, various catalyst/support structures have been synthesized but there are still few methods for scaling-up production of electrocatalysts with many active sites. The progress in engineering nano, micro, and macroscale structure of catalysts shows the effectiveness of this strategy for designing HCD catalysts.

3.4. Path for Electron Transport

Constructing electron transport path to reduce electrical resistance is another strategy to obtain good HCD performance of catalysts by 1) changing the rate of electron transport in catalyst and 2) changing the electron transfer mode from the conductive support to the catalyst-electrolyte interface (Figure 6c). To reduce these electrical resistances, researchers focus on several strategies that change electron transport from support to catalytic sites, including electron transport in a conductive catalyst, electron transfer at catalyst-support and catalyst-catalyst interfaces, and electron transport mode in a semiconducting catalyst.

Using materials with high electrical conductivity as the catalysts or supports is a general idea to improve catalytic performance at HCDs. The materials include carbon, metals, and some metallic compounds. There are several ways to change the conductivity of materials, such as phase engineering and defect engineering. A main challenge is to use high conductivity and meanwhile to get high intrinsic activity. Recently, Yang et al. directly grow a metallic 2H-phase Nb₁.₃₅S₂ catalyst on a highly-conductive glassy carbon support (Figure 9a), where it shows a conductivity of 10³ S cm⁻¹.[25] This conductivity is comparable to the bulk 3R-NbS₂ and only an order of magnitude lower than Pt metal. Interestingly, the intrinsic activity of Nb₁.₃₅S₂ catalyst is higher than bulk 3R-NbS₂ and is comparable to that of Pt wire. As a result, it has an excellent HCD performance with an overpotential of about 370 mV at a current density of 5000 mA cm⁻² normalized by the projected surface area of catalyst for the HER (Figure 9b,c). For OER catalysts, due to the oxidation potentials usually convert metallic materials into (hydro)oxides, the conductivity of catalysts and their performance at HCDs may be changed.[30] It is reported that a proper content of defects or vacancies in metal oxides could increase
their electrical conductivities. For example, Bao et al. show that rich oxygen vacancies in ultrathin NiCo$_2$O$_4$ nanosheets promote their OER reactivity and the delocalized electrons around the oxygen vacancies are easy to be excited to the conduction band to enhance the conductivity of catalyst.[55] The catalyst therefore delivers a current density of 285 mA cm$^{-2}$ at an overpotential of 320 mV. Besides, despite many studies on the design of electrocatalysts using materials with good conductivity, it is still not known whether the better electrical conductivity the better HCD performance or there is a critical value of the electrical conductivity above which a higher conductivity does not result in a better HCD performance.

Boosting electron transfer through catalyst-support and catalyst-catalyst interfaces directly improves the catalyst performance for HCD water splitting. Indeed, the interfacial resistance is smaller between a metallic catalyst and a conductive support than that of semiconducting or insulating catalyst. Based on this, self-supporting catalysts/electrodes that use a support such as metal foam and carbon material with catalytic materials directly grown on its surface are intensively studied.[107,108] Coupling effects between a catalyst and its support may inject or withdraw electrons from the catalyst, and thus changing the interfacial resistance.[83,109] To reduce this resistance, the thickness or size of catalyst is crucial, especially for semiconducting catalysts.[29,68] Moreover, the electron transport paths should be short, which requires a small thickness/size of the catalyst building blocks and their proper stacking. For example, Yan et al. show that interface between electrodeposited catalyst materials (cerium dioxide and nickel hydroxide) and support materials (graphite with nitrate inserted

Figure 9. Engineering the electron transport paths of catalysts for HCD water splitting. a–c) Metallic 2H-phase Nb$_{1.35}$S$_2$ catalyst with a high electrical conductivity grown on a glassy carbon support. Reproduced with permission.[25] Copyright 2019, Springer Nature. d,e) 2D MoS$_2$ nanosheets showing a semiconducting-to-metallic state transition at HCDs. Reproduced with permission.[68] Copyright 2020, Springer Nature.
into its layers) becomes strong due to charge transfer between them, which results in a highly porous and high-loading film via proper stacking.\textsuperscript{[108]} The catalyst exhibits an overpotential of 310 mV at 1000 mA cm\textsuperscript{−2} and a durability over 300 h.

Some semiconducting materials are also used for HCD water splitting and their electron transport mode is found to be interesting.\textsuperscript{[14]} Usually, a semiconducting catalyst needs to be combined with a conductive support for use and thus showing a three-phase electrochemical interface that consists of a catalyst, a conductive support, and the electrolyte. The electron transfer mode is different to that for metallic catalysts. Recent studies have shown that electrons transfer directly from the conductive support to the catalyst surface along the three-phase contact lines.\textsuperscript{[88,110]} He et al. find that the surface of 2D MoS\textsubscript{2} nanosheets even shows a metallic state as current density increases while the bulk region remains semiconducting (Figure 9d,e).\textsuperscript{[88]} Altogether, these results indicate that constructing-efficient electron transfer path is necessary to achieve good catalytic performance for HCD water splitting.

3.5. Catalyst-Electrolyte Interplay

The interaction between the catalyst and the electrolyte (or reactant) has received great attention in recent years because it affects our fundamental understanding about the catalytic sites in operating conditions. The HCD performance of catalysts is tuned by engineering catalyst-electrolyte interplay by 1) changing bond strength between intermediates and active sites, and 2) changing mass transfer efficiency (Figure 6d). Different to surface adsorbents, the species involved in the catalyst-electrolyte interplay are directly derived from the electrolytes or reactants during reactions. Several strategies have been developed to take use of catalyst-electrolyte interplay toward better HCD performance, including engineering the interaction between catalyst and interfacial water in inner Helmholtz plane (IHP), engineering the adsorbents in the IHP, taking use of the HCD performance, including engineering the interaction between catalyst and interfacial water in inner Helmholtz plane (IHP), engineering the adsorbents in the IHP, taking use of the HCD performance, and hence tunes the HCD performance of the catalyst. For example, Ledezma-Yanez et al. report that adding nickel to a Pt(111) surface accelerates the reaction rate of HER in alkaline media.\textsuperscript{[112]} They attribute the different activities of Pt(111) and nickel decorated Pt(111) to the reorganization of the interfacial water that accommodates charge transfer through the electric double layer. The energetics are controlled by the strength of the interaction between water molecules and the interfacial field. In another work, Jin et al. report that Ni-SN@C facilitates water adsorption and weakens hydrogen adsorption, leading to the generation of hydronium ions near the surface of the catalyst in a high-pH electrolyte. In contrast, on the Ni@C and Ni\textsubscript{3}N catalysts, the H\textsuperscript{+} would be directly converted into hydrogen molecule instead of forming hydronium as the intermediate at HCDs. The interaction between catalyst and interfacial water in the IHP can influence the reaction mechanism and activity.

Second, adsorbents in the IHP on catalyst surface affect the rupture/formation of chemical bonds, stabilization of intermediates, etc. Their roles in the catalytic performance have recently aroused interest.\textsuperscript{[24,84,113]} For example, Zhang et al. construct a highly conductive edge-enhanced Ni\textsubscript{0.2}Mo\textsubscript{0.8}N/Ni hybrid catalyst, which delivers 300 mA cm\textsuperscript{−2} at an overpotential of 70 mV for HER in 1 m KOH.\textsuperscript{[39]} This good HCD performance is attributed to tip-enhanced-like local electric field around the topmost Ni nanoparticles, leading to an increased concentration of K ions in the IHP. The types of surface adsorbents may be affected by the applied current densities or overpotentials, resulting in a different catalytic performance at HCDs. Very recently, Nong et al. find that the coverage of holes is changed with a change in overpotential and is coupled with deprotonation of the IrO\textsubscript{2} catalyst for OER.\textsuperscript{[64]} The local adsorption of a high concentration of reagents on a catalyst during reactions changes the chemical potential and hence HCD performance.\textsuperscript{[90]} Engineering the coverages or types of adsorbents on catalysts for HCD water splitting deserves more attention in future.

Third, the pH value of the electrolyte is found to influence the HCD performance of catalysts.\textsuperscript{[63]} For example, Luo et al. show that Mo\textsubscript{2}C nanoparticle catalysts are modified by different types of surface oxygen species as the pH value changes.\textsuperscript{[24]} Specifically, O\textsubscript{2}-group is prone to modify Mo\textsubscript{2}C surface when pH value is high while OH-group is found at surface at low pH conditions. The former one shows a relatively lower energy barrier for water dissociation than unmodified Mo\textsubscript{2}C, and the latter one shows a lower energy for adsorption/desorption of hydrogen. As a result, such a catalyst exhibits a current density of 1000 mA cm\textsuperscript{−2} at overpotentials of 220 and 227 mV in electrolytes of pH = 14 and pH = 1, respectively. In another work, Yoon et al. report a catalyst composed of polycrystalline CoP and oxygen-enriched amorphous Co-O-P that keeps its hybrid crystalline-amorphous phase in acidic and neutral electrolytes, but reconstructs into the crystalline CoP and Co(OH)\textsubscript{2} in alkaline electrolyte.\textsuperscript{[42]} The pH value of electrolyte affects the phase and morphology of catalysts, resulting in excellent HER performance at a wide range of pH values. Therefore, pH value of electrolyte needs to be considered when engineering HCD performance of catalysts. Note that the studies of the roles of catalyst-electrolyte interplay in HCD electrocatalysis need to be combined with advanced in-situ spectroscopy characterization to help researchers to understand HCD catalysis in real operating conditions.

4. Multiscale Design of Catalysts toward HCD Electrocatalysis

The five aspects discussed above are used to engineer catalysts to achieve efficient HCD water splitting. The engineering of any single aspect cannot produce catalysts with a superior HCD performance, and hence a multiscale design strategy for catalysts that engineering several aspects at the same time is necessary. This design strategy has recently been used to achieve high-performance catalysts under the HCD conditions.\textsuperscript{[49,114-119]} For example, Yang et al. recently show that a Pt/Ni-Mo electrocatalyst only needs an overpotential of 113 mV to reach an ultrahigh current density of 2000 mA cm\textsuperscript{−2} in the saline-alkaline electrolyte and can run at 2000 mA cm\textsuperscript{−2} for 140 h without
performance decay.\textsuperscript{[20]} Such an excellent performance at HCDs can be attributed to the multiscale design strategy of catalyst that takes consideration of surface chemistry of the catalyst, electron transport pathway, and catalyst morphology in the design. Despite progress has been made in the multiscale design strategy of catalysts for HCD water splitting, there are some points need to be developed.

To optimize the multiscale design of catalysts for HCD electrocatalysis, the relations between the five factors need to be comprehensively considered because there may be many trade-offs. Here are some examples. A low-dimensional catalyst has a large number of exposed catalytic sites, which however may lower the rate of mass transfer because the effective diffusion length may be increased due to its higher sinuosity. The catalyst film assembled by low-dimensional catalysts may also decrease the electrical conductance of the film by introducing too many catalyst-catalyst interfaces. The small sizes of low-dimensional catalysts may also reduce their stability due to a numbers of surface unsaturated atoms. Presence of the surface adsorbents and spectators on catalysts may destabilize the reactants and stabilize the intermediate to produce a higher intrinsic activity, however, they may also cover some catalytic sites giving a lower electrochemical surface area and producing an interfacial resistance. A catalyst with an ultrahigh surface area has a large number of catalytic sites, but this may increase the transport resistance of gas or ions at HCDs. Based on the above discussions, the multiscale design strategy of catalysts for HCD water splitting is complicated in practice because some relations between the main factors need to be balanced. There is still a plenty room for the further development of the multiscale design of HCD electrocatalysts.

5. Conclusions and Perspectives

In this review, the effects of HCD conditions on local reaction environment and catalytic performance have been discussed firstly. By discussing recent advances in HCD electrocatalysts, several key aspects that have been used for engineering catalysts toward efficient HCD water splitting have been then summarized, including low dimensionality of catalysts, surface chemistry electron transport path, morphology, and catalyst-electrolyte interplay. Finally, we highlight the multiscale design strategy of efficient HCD catalysts. The performance of state-of-the-art HCD electrocatalysts is still far from their target values. Therefore, it is still crucial to explore HCD electrocatalysts for the industrial applications. Several research directions should be pursued in future.

5.1. In-Depth Understanding About Electrochemical Interfaces under HCD Conditions

The local electrochemical environment at electrochemical interface is greatly affected by current densities. However, mechanism understanding about electrochemical interface under HCD conditions is still limited, hindering the rational design of high-performance electrocatalysts for water electrolysis working at industrially-relevant HCDs. In situ spectroscopic characterization and other advanced characterization techniques need to be developed to understand how HCD affects the electrochemical interfaces and processes, which however, are very challenging as generation of gaseous bubbles is violent at HCDs and they may scatter rays. Besides, theoretical methods that are suitable for HCD conditions need to be developed.

5.2. Developing Multiscale Design Strategies for HCD Electrocatalysts

The performance of HCD electrocatalysts is determined by several aspects at atomic, nano-meter, and micro-meter scales. To obtain efficient and stable HCD catalysts, multiscale design strategies need to be developed that consider all the aspects at the same time. And the trade-off in activity and stability of HCD catalysts caused by these aspects need systematic studies. It is crucial to explore strategies for OER catalysts at HCDs that show smaller overpotentials than target values, such as the middle-term target values for alkaline OER is 1.43 V at 500 mA cm\(^{-2}\). Currently, excellent performance at HCDs have been shown by some “self-supporting” catalysts in alkaline electrolyzers and H-cells, where the catalytic materials are grown on porous and conductive substrates.\textsuperscript{[20,116]} Great efforts are expected to develop multiscale design strategies for HCD catalysts suitable for electrolyzers based on ion exchange membranes. Stability of OER catalysts under acidic environment at HCDs is important. It should also be noted that as compared to HER catalysts, the design of OER catalysts at HCDs is more challenging, due to its slower reaction kinetic, lower diffusion coefficient of OH\(^-\) than H\(^+\), and effects of pH value and local environment.

5.3. Developing Standards for Evaluating Catalyst Performance Relevant to Industrial Use

This requirement calls for the benchmarking and assessment of catalytic performance using standardized materials and conditions, and moreover, under industrially-relevant conditions.\textsuperscript{[60,120]} The key performance metrics need to be identified to assess the catalyst performance under HCDs, that call for metrics beyond the commonly used ones for catalysts at low current densities. For instance, \(R_m\) was used as an indicator to evaluate the performance of a catalyst at HCDs that take kinetics and mass transferability into consideration.\textsuperscript{[24]} Moreover, electrolyzers with similar configurations used in practical applications should be used for assessment of HCD catalysts. For industrial PEM and alkaline electrolyzers, electrode sizes are at the scale of square meter, while those used in the laboratory are typically with sizes of square centimeter or smaller. A recent work shows that a small electrode size leads to an uneven distribution of electric field and different mass transport behaviors with large electrode, and thus catalytic performance on a small electrode cannot be translated into those with large sizes at HCDs.\textsuperscript{[105]} Issues such as electric field distribution, mass transport efficiency, and thermal management, should be considered for electrodes with square meter scale.
sizes for HCD water splitting. In addition, more efficient and
time-saving stability and durability test methods are needed.

5.4. Economic Considerations for the Future Development of
HCD Electrocatalsysts

Beyond these scientific and technological issues, the economic
considerations are necessary for the future development of
HCD catalysts. To achieve large-scale implementation of HCD
reactions, green productions, and costs of the technologies,
including raw materials/chemicals, production costs of cata-
lysts, and the energy consumption during electrochemical reac-
tions, need to be considered.

We project continued endeavors toward the development of
efficient catalysts for the electrochemical water splitting tech-
nologies and their wide implementation under the HCD condi-
tions would make them gaming-changing players toward global
carbon neutrality and sustainable development future.

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Conflict of Interest

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