Strain Engineering in Electrocatalysts: Fundamentals, Progress, and Perspectives

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Strain engineering of nanomaterials, namely, designing, tuning, or controlling surface strains of nanomaterials is an effective strategy to achieve outstanding performance in different nanomaterials for their various applications. This article summarizes recent progress and achievements in the development of strain-rich electrocatalysts (SREs) and their applications in the field of electrochemical energy conversion technologies. It starts from the definition of lattice strains, followed by the classification of lattice strains where the mechanisms of strain formation and the reported methods to regulate related strains are elaborated. The SRE characterization techniques are overviewed, focusing deeply on the clarification of the strain-property relationship of these SREs. Their applications for different electrocatalytic reactions are further highlighted, including the hydrogen evolution reaction, oxygen reduction reaction, oxygen evolution reaction, alcohol oxidation reaction, electrochemical carbon dioxide reduction reaction, and nitrogen reduction reaction. Related reaction mechanisms of the SREs are interpreted after taking catalytic performance, as well as the relationship between the SRE properties and their strains into account. The challenges and future opportunities to regulate SREs are finally outlined and discussed together with their potential applications in different fields.

1. Introduction

Energy crisis and environmental pollution are two major challenges occurring currently in our society, mainly due to the extensive utilization of fossil fuels. The design and development of efficient, economic, and sustainable strategies to convert clean energy (e.g., solar energy, wind energy, and hydropower energy) is thus of great significance. Among various available strategies, electrochemical energy conversion technologies have been attracted extreme attention. They mainly include (photo)electrochemical reduction of atmosphere-rich and greenhouse gas—carbon dioxide—into high value-added chemicals or liquid fuels under mild reaction conditions, electro-synthesis of NH3 with low energy consumption to substitute the Haber method, electrochemical overall water splitting, and different kinds of fuel cells. By use of these electrochemical energy conversion technologies, it is believed that both the issues of energy shortage and environmental pollution are promising to be solved, eventually creating a globalized system with a sustainable energy circle for our society in the future (Figure 1).[1–7]

To achieve efficient electrochemical conversion technologies, high-performance electrochemical conversion platforms need to be initialized, where electrocatalysts are frequently required. An electrocatalyst actually plays a vital role in the determination and further improvement of reaction rate, efficiency, and selectivity of different electrochemical transformations. In terms of its catalytic performance, the most crucial factors are generally considered as the amount of its active sites, the intrinsic activity of each active site, and the total efficiency of these active sites.[8] It is well-known that the amount of active sites of an electrocatalyst and its electrocatalytic efficiency can be increased through enlarging the surface area of an electrocatalyst, for example by means of synthesizing a nanostructured catalyst (e.g., nanosheets,9) nanowires,10) nanopores,11–13) and core–shell structures14,15). Meanwhile, the intrinsic activity of each catalytic site basically follows the Sabatier principle,16–20) which is closely related to the ability of an electrocatalyst to weaken or strengthen the binding energies with reactants, reaction intermediates, and/or products. For example, when the free energy of hydrogen adsorption (ΔG_H) on the active sites of an electrocatalyst remains at a moderate strength, this catalyst exhibits the highest catalytic activity toward hydrogen evolution reaction (HER). In contrast, too strong or too weak ΔG_H on the active sites of an electrocatalyst precludes the HER.21–23)

Among numerous electrocatalysts, multiple metal components based electrocatalysts have been extensively utilized in...
various energy conversion technologies. As one of the state-of-the-art electrocatalysts, they feature many unique physical and chemical properties.\[^{24-26}\] Prior to achieving their superior electrocatalytic performance, the disclosure of the structure-activity relationship of different electrocatalysts is always fundamentally important. In this regard, several theories have been proposed to describe such complicated structure-activity relationship, covering ligand effect,\[^{27-30}\] electronic effect,\[^{31-33}\] synergistic effect,\[^{34-37}\] and strain effect.\[^{38-41}\] Taking the ligand effect as an example, it refers to that the electronic structure of a catalytic site is affected by the neighbor atom, leading to different d-band electronic structures and adsorption ability of each catalytic site. The electronic effect suggests that the electronic density of a catalyst is affected by the electronic transform between a support and a catalyst particle. In consequence, the catalyst features changed catalytic performance when different supports are applied. The synergistic effect generally appears on a catalyst surface with multiple active sites, where all of them participate in the investigated reactions, resulting in their better catalytic performance than individual catalytic sites. The strain effect, the topic of this review, is different from those mentioned effects. It is aroused by the change of atom-atom bond length or by the induced lattice mismatch. In this case, the catalyst with a strain effect may even have a diverse electronic structure.\[^{42}\] The adsorption ability of the active sites toward reactants, reaction intermediates, and/or products changes accordingly. Therefore, the performance of such a strain-rich electrocatalyst (SRE) toward different reactions such as HER, oxygen reduction reaction (ORR), oxygen evolution reaction (OER), alcohol oxidation reaction (AOR), electrochemical carbon dioxide reduction reaction (ECO2RR), and nitrogen reduction reaction (NRR) is tunable or can be regulated.

It is quite obvious that rational design and optimization of different SREs is the base to experimentally verify these proposed theories. Meanwhile, the strain effect has been proved to be quite useful and effective in the catalyst design and optimization within those proposed effects in that the adsorption nature and catalytic performance of a SRE can be regularly and efficiently modified by its lattice strain. In general, a strain commonly exists in a core–shell structured catalyst, mainly stemming from the lattice mismatch of different atoms in the core and the shell.\[^{43}\] For example, a compressive strain appears in the Pt (111) shell of a PtNi@Pt catalyst,\[^{44,45}\] while a tensile strain is found in the Pt (111) shell of an Au@Pt catalyst.\[^{46}\] The former has been revealed to be beneficial for the ORR, while the latter boosts methanol oxidation reaction (MOR) and

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Figure 1. Schematic diagram of a globalized system with a sustainable energy circle for our society in the future by use of different electrochemical conversion technologies.
ethanol oxidation reaction (EOR). In short, to design and synthesize the catalysts with the adjustable adsorption ability via strain engineering, accurate control of the strain states during the synthesis process of the catalysts, precise characterization of the strain intensities of the SREs, and deep clarification of inherent mechanisms of the strain regulation are of great importance from fundamental and practical viewpoints. More importantly, discovering and understanding the relationship between the electrocatalytic reaction mechanisms of the SREs and related strain regulation theories is expected to lead to more efficient SRE design and eventually much improved electrochemical conversion performance of different SREs.

With an aim to provide a comprehensive account of lattice strains, as well as, to address both computational and experimental aspects of strain effects, recent advances on engineering the strains of different electrocatalysts are summarized in this review. In its first section the fundamentals, structural classification, strain-rich support to load single-atom catalysts, the stability of SREs, characterization techniques of lattice strains, and how strain affects the catalytic performance are introduced. With aid of theoretical predictions and experimental proofs, special attention is paid to systematic contribution of strain engineering of numerous SREs for several electrocatalytic applications. In the second section, recent progress and achievements of these SREs to promote the ORR and HER are highlighted, where the related relationship between reaction activities of different SREs and the adsorption energies of reaction intermediates on these SREs is revealed. The applications of SREs toward OER, AOR, ECO2RR, and NRR are also highlighted, where the related relationship between reactions of SREs and the synthesis process of the catalysts, precise characterization and applications of various reported SREs, but also recent achievements that have been well summarized up to date, including the results about the strain-rich supports to load single-atom catalysts, mathematic simulation of surface strain, the HER performance of SREs in alkaline solutions, and the stability of SRE.

2. Fundamentals of Strain in Electrocatalysts

2.1. Strain Formation Mechanisms

A lattice strain refers to an atom-atom distance on the particle surface or a local area, which can be either larger or smaller than a standard atom-atom distance in a bulk material. The strain intensity is defined as:

\[ \varepsilon = \left( \frac{d_p - d_r}{d_r} \right) \]  

where the term of \( d_p \) stands for an atom-atom distance on the particle surface or a local area, the term of \( d_r \) refers to a standard atom-atom distance in a bulk material. In this context, a catalyst consisting different atoms is possible to have a compressive or tensile strain effect. The inducement of those two strains in the catalysts reported up to date can be defined as the lattice mismatch in the core–shell structured catalysts, supported particles/cluster catalysts, defects, size/shape variation, and solid alloys with dopants (Figure 2). In the following section, these five kinds of strain formation mechanisms are discussed. The synthesis methods of related SREs are also included in this section.

2.1.1. Strain in Core–Shell Structured Catalysts

In a core–shell structured catalyst, the lattice parameters of one metal in the core and another metal in the shell are inevitably different. In some cases, the lattice parameters of the core and shell metals have slight discrepancies. Consequently, a change of lattice shape exists at the interface between the core and the shell. The strain state in the shell is complex and affected by many factors, namely including lattice mismatch between the core and the shell, the thickness and growth method of the shell, and the shape of the core. When the interface between the core and the shell is a smooth plane, the lattice of the thin shell tends to be consistent with the lattice of the core. In other words, the larger lattice constant side tends to be compressive, while the smaller lattice constant side tends to be tensile (Figure 3a). With an increase of the thickness of a shell, the surface Gibbs energy tends to reach the minimum, the strain states are thus decreased through the formation of defects (e.g., the glide of dislocation segments on the Ge@Si interface) (Figure 3b). In other words, the strain at the interface between the core and the shell might be the strongest. The lattice strain state in practical core–shell nanoparticles is also affected by the epitaxial growth method of the shell. For the Pt shell epitaxial growth on the Pd nanocube core, when the surface diffusion velocity \( V_{\text{diffusion}} \) is larger than the atom deposition velocity \( V_{\text{deposition}} \), the Pd shell intends to be spread on the Pd (100) surface layer-by-layer (Figure 3c). In this context, the Pt skin on the Pd (100) surface is compressive and in line with the plane model (Figure 3d). When the \( V_{\text{diffusion}} \) is smaller than \( V_{\text{deposition}} \), Pt atoms intend to stay at the corner sites and form a Pd-Pt concave nanocube. The high-index facets are formed and the strain state is thus different from the plane model (Figure 3e). In a core–shell nanoparticle with a shaped surface, the strain states in the corner and edge are also different from those on the surface. For a Pd@Pt core–shell icosahedral, the nonuniform compressive strain is observed on the Pt shell (Figure 3f). Differently, for a Pd@Pt core–shell octahedron, the compressive was observed on the corner while tensile strain was observed on the surface and edge (Figure 3g). In the strain state simulation of ideal epitaxial growth of Pd atoms on an Au nanocube via the layer-by-layer approach, it was found that the Pd shell on the face of Au nanocube is stretched while the Pd shell on the edges and corners is compressive. Besides, the stacking faults near the corner of the Au-Pd interface were observed.

The nanomaterials with a core–shell structure and adjustable lattice strain have been widely studied as electrocatalysts. This is partially because the thin shell is exposed on the surface completely, and the efficiency of shell catalysts is enhanced. Note that the growth of shell catalysts on the shaped core tends to stay at
the unsaturated coordinated corner, edge, terrace, or step sites at the beginning of growth, which may decrease the atomic efficiency of the shell however increase the reaction activity. For the growth of Pt shell on Pd nanocube core, the Pt atom can stay at the corner when the reduction temperature is 170 °C (corner protected Pd@Pt, CPNC, Figure 3h), while the Pt atom tends to disperse to the Pd nanocube surface uniformly when the reduction temperature is 180 °C (regular nanocube Pd@Pt, RNC, Figure 3i). By increasing the reduction temperature (among 170–180 °C), the Pt atom in the corner is less than CPNC but more than RNC. In other words, some Pt atoms are redistributed to (100) terraces of Pd core for near 1–2 layers (modified nanocube Pd@Pt, MNC, Figure 3j). The MNC ($0.42 \text{ mA cm}^{-2}$) not only shows higher specific activity than CPNC ($0.37 \text{ mA cm}^{-2}$), RNC ($0.17 \text{ mA cm}^{-2}$), and Pt/C catalyst ($0.17 \text{ mA cm}^{-2}$) toward ORR but also shows lower activity loss ($0.37\%$ of CPNC) during the stability test than CPNC ($3.65\%$), RNC ($6.09\%$), and Pt/C ($21.51\%$) catalyst.[74] The design of the core–shell SREs must also consider other facts, such as, the exposed facets, ligand effect, and electron transform caused by the core. The exposed crystal facets of the shell are possible to be controlled by tuning the shape of a metal core once an epitaxial growth mechanism is applied. One typical example is the epitaxial growth of an Ir layer on a Pd-nanocube core, where the exposure of Ir (100) facet was realized (Figure 3k). Differently, the growth of this Ir shell on a Pd octahedra resulted in the exposure of Ir (111) facet (Figure 3l).[75] As for the core–shell SRE with a thin layer, its catalytic performance is also affected by the ligand effect of the core. In a L10-CoPt@Pt SRE, the number of atomic Pt layers in the shell was tuned to be 2–3 (Figure 3m).[76] This L10-CoPt@Pt SRE exhibited lower ORR overpotential than Pt nanoparticles and L10-CoPt@Pt SRE with a thicker Pt shell. As clarified experimentally and theoretically, the superior ORR performance on this L10-CoPt@Pt SRE was due to the combination of compressive strain and ligand effect of Co atoms in the core. Meanwhile, it has been demonstrated that the electron transform between the core and the shell is caused by the difference of their work functions in the core–shell electrocatalysts. Such an electronic effect was also probably involved during the investigated electrochemical reactions. Likewise, the HER overpotential of an Au@CoP SRE was smaller than that of pure CoP nanoparticles. Due to the electronic transform from the CoP shell to the Au core, the CoP layer coated on the Au core was found to have a lower electron density than a standard CoP-layer.[77]
The regulation of strain state is crucial for core–shell catalyst design. In general, the strain state of the shell layer can be regulated by choosing an alloy with an adjustable lattice parameter as the core. For example, the Pt shells grown on the core of a CoM (M = Mn, Fe, Ni, Cu, Zn) intermetallic alloy exhibit different Pt strain states, stemmed from the varied lattice constants of the CoM cores. In other words, the strain states of the Pt shell in these core–shell structured catalysts are effectively controlled. Among those CoM@Pt catalysts, the CoNi-alloy-core-Pt-shell catalyst (named as L10-CoNi@Pt) that possesses the suitable lattice difference between the core and the shell exhibits a mass activity of 3.1 A mg⁻¹Pt toward ORR, which is 31 times of commercial Pt/C.[78] Besides, the strain state can be adjusted by changing the layer number of the shell. It has been revealed that the strain state in a core–shell structured catalyst weakens when the layer number of a shell increases. For instance, the Ir—O bond length in a thicker IrOₓ shell that is coated on the core of IrCo alloy nanowires (IrCo@IrOₓ) is longer than that in a thinner IrOₓ shell. Namely, the intensity of the compressive strain in the IrOₓ shell is weakened when the layer number of the IrOₓ shell is increased. Stemming from a suitable strain state of an IrCo@IrOₓ electrocatalyst with a three-layered IrOₓ shell, its OER overpotential was smaller than other IrCo@IrOₓ electrocatalysts.[79]
The strain state of the Pt shell can also be controlled by regulating the volume of the core metal in a core–shell Pd@Pt electrocatalyst. A two-step reduction method was applied to synthesize the Pd@Pt nanocubes, of which size was 18 nm. The phosphorization of the Pd core of the Pd@Pt nanocubes was then conducted in a mix OAm/TOP (11:1) solution at 250 °C for 120 min. The Pt shell was found to be stretched, due to the size expansion of the Pd core during its phosphorization (namely, the transform of Pd to Pd-P) (Figure 4a). On the contrary, the compressive strain in the Pt skin was achieved when P atoms in the Pd-P@Pt nanocubes were removed via the treatment in OAm solution at 250 °C for 60 min (Figure 4b). The lattice strain states of the Pt shell were thus well controlled in the range of −5.1% to +5.9%.

It is noted that the lattice of the shell is equi-biaxial tensile or compressive when the core is also fcc metal, such as, the Pt shell in a Pd@Pt nanoparticle is equi-biaxial compressive (Figure 4c). However, when the core is an alloy featuring a fct phase (e.g., PtFe, PtCo, PtNi), anisotropic strains exist in the Pt shell (Figure 4d). In other words, the strains are different along two directions. By rational design of the alloy elements of the core, both tensile and compressive strain can be achieved in the shell. The anisotropic strains are thus important in the SRE design.

To synthesize core–shell structured catalysts, the most common approach is the so-called epitaxial growth method. Taking a seed growth method as an example, it is especially effective since the nucleation step has the highest energy barrier for the reduction and growth of metal ions. When a metallic core already exists in the solution, the ions tend to grow on this metallic core rather than to form new cores. In addition, the shape and the exposed surface (or facets) of the shell can be induced and controlled, depending on the shape of the core. For example, a series of core–shell structured catalysts has been constructed by use of such an approach, such as Pd@Pt octahedron, Pd@Pt nanocube, and Pd@Pt icosahedron. Differently, the shell can be electrochemically deposited on the core. For example, Pt layers have been electrodeposited from a K2PtCl4 solution on an Au core. Up to used electrodeposition method (e.g., constant current, constant potential), electrodeposition potential/current density, and electrodeposition time, the numbers of these Pt layers or the amount of active Pt sites have been well controlled.

In addition to an epitaxial growth approach, the core–shell structured catalysts have been synthesized by a one-pot reduction method, where reduction reactions of metallic ions for the core and the shell sequentially occur. In the first step, one metal with a lower reduction potential is reduced to form the core. Subsequently, another metallic ion with a higher reduction potential is reduced and deposited on the core. For instance, the reduction potential of Pt(II) ions (1.18 V vs standard hydrogen electrode, SHE) is higher than that of Pd(II) ions (0.95 V vs SHE). When both Pd(II) and Pt(II) ions exist in a reduction solution (e.g., ethylene glycol), the Pt(II) ions are reduced into Pt metal atoms in the first step. As the core, these Pt atoms are coated with a shell of Pt atoms or a Pt layer that are reduced from Pt(II) ions in the following step. Using this one-pot method, as-synthesized Pd@Pt catalysts have an expected core–shell structure, where a layer number of the Pt shell (skin) is about 2 (Figure 4f–i).

![Figure 4](image-url)
In addition to these methods, the core–shell structured catalysts have been obtained from the alloyed catalysts, where surface atoms are selectively de-alloyed. For example, a bunched PtNi nanoalloy has been synthesized by the co-reduction of Pt(II) and Ni(II) ions with oleylamine in the first step, followed by wet-chemical removal of the surface Ni atoms from this PtNi alloy by use of the corrosive HNO3.[44] An as-obtained catalyst had a PtNi-alloy core and a Pt shell, where the Pt skin is compressive. This catalyst exhibited excellent ORR activity (e.g., low ORR onset potential and half-wave potential). Meanwhile, the selective dealloying process has been achieved by an electrochemical stripping method. For example, Bi atoms in the PtBi@Rh core–shell structured nanoplates have been first dissolved by means of cycle voltammetry in the HClO4 electrolyte within a potential range of 0.05 to 1.1 V (vs reversible hydrogen electrode, RHE) (Figure 4j). The tensile strain was found in the as-synthesized PtBi@RhPt catalyst. This PtBi@PtRh model catalyst showed enhanced EOR catalytic activity and C–C bond cleavage ability.[85]

2.1.2. Strain Caused by the Support

The interaction between a cluster and a support has been found to significantly affect the catalytic performance of an as-formed catalyst. This results from the fact that in a metallic cluster its local lattice mismatch and electronic structure are dramatically influenced by the support. Actually, the formation mechanism of the strain in a supported cluster is similar to that in a core–shell structured catalyst. The strong interaction with an obvious lattice mismatch between a support and a cluster leads to a high lattice strain. For example, through the control of the lattice parameter of the used support, Pt nanoparticles with adjustable Pt-Pt atomic distances have been synthesized.[54] The Pt nanoparticles supported on the Li0.5CO (Li0.5CoO2) and LCO (LiCoO2) supports have similar lattice parameters, although the lattice parameters of the two supports are different. When Li(I) ions are extracted from the Pt/LCO catalyst and further transformed to the Pt/Li0.5CO catalyst, the Co-O layer space of LCO is enlarged from 0.469 to 0.482 nm. The corresponding crystal lattice of supported Pt nanoparticles has been found to be affected by the Co-O layer space. The catalyst with a larger Pt-Pt distance and a tensile strain is formed when the Co-O space is improved (Figure 5a). On the contrary, when Li(I) ions are intercalated into the Pt/Li0.5CO catalyst, the Co-O layer space is decreased from 0.482 to 0.469 nm, making the supported Pt nanoparticles have a compressive strain (Figure 5b). Therefore, both tensile and compressive lattice strains of Pt nanoparticles have been effectively synthesized. In another case, the Ni branches were synthesized by means of the seed growth method in the first step, followed by the growth of Pt clusters on the surface of Ni branches.[52] The variation of the growth time of Pt clusters leads to the controllable synthesis of Pt clusters with different sizes (e.g., 1.9 or 2.7 nm) (Figure 5c). Since the lattice parameter of a Ni support (2.48 Å) is smaller than that (2.81 Å) of a Pt support, a compressive strain is found in the Pt clusters, obviously originating from the strong interaction between the Ni support and Pt clusters. When the size of Pt clusters is enlarged from 1.9 to 2.7 nm, the compressive strain is decreased from 5.5% to 3.8%.

The Pt clusters with a size of 1.9 nm exhibited higher HER activity than those with a size of 2.7 nm. For a carbon-supported Fe2P catalyst (Figure 5d), the compressive strain is produced in FeP2, stemming from the lattice mismatch between FeP2 and the carbon support. Such a FeP2 catalyst with a compressive lattice strain exhibited lower OER overpotential and enhanced stability than a FeP2 catalyst without a carbon support (namely a FeP2 catalyst features no strain).[55]

The strain distribution of the supported catalyst is actually affected by the used support. For example, the compressive strain of a PtNi@Ti3C2 catalyst (namely, the PtNi alloy nanoparticles supported on the Ti3C2 nanosheets[86]) is distributed on the edge of the particles when it is compared with the PtNi catalyst (namely the PtNi alloy nanoparticles without supports). This is probably attributed to the surface-induced interaction between the catalyst and the support. In other words, the lattice strain of nanoparticles or clusters is based on lattice mismatch of the cluster and the support, which is introduced by the strong interaction between the support and the catalyst.

2.1.3. Strain Caused by Defects

The strain in defect-rich catalysts[88–91] is different from the lattice strain caused by the lattice-mismatch. In this case, the atom-atom bond length is affected by the defect sites nearby. It is well demonstrated that defects widely exist in solid materials and play an important role in determining the properties of these solid materials. The defects can be generally divided into point defects, line defects, planar defects, and bulk defects.

In general, point defects are in the form of vacancies. For example, the Se vacancy exists in the NbSe2 alloy, where the vacancy of the Se atom makes other atoms near the Se vacancy shift to the vacancy site (Figure 6a).[92] The tensile strain is then generated near the Se vacancy site (Figure 6b). In porous Pd nanosheets, the existence of the Pd vacancy (Figure 6c) is seen in the Pd nanosheet,[93] which results in the strained Pd nanosheets featuring superior catalytic ORR performance (e.g., lower overpotential and better stability) over a Pt/C commercial catalyst. The 2d MoS2 based nanomaterial are potential electrocatalysts in HER (Figure 6d). The theoretical calculations revealed that in the MoS2 catalyst the value of ΔGf is highly relative to the tensile strain state and the concentration of the S vacancy.[94] The strain in MoS2 can be introduced by S vacancy, Mo vacancy, and atom doping.[95]

The planer defects are usually shown in the form of dislocations or in the grain boundaries, where the symmetry of material is destroyed and thus the local lattice strain mismatch appears. For example, a planer defect-rich Ru nanoparticle (L-Ru) has been prepared by laser irradiating of a Ru target (Figure 6e).[96] The L-Ru catalyst has a smaller Ru-Ru atomic distance (0.233 nm) than standard Ru powers (0.236 nm). Namely the grain boundaries lead to a compressive strain of Ru nanoparticles. The PdAu nano-chains have been synthesized via the galvanic replacement of the template of Co nano-chains with Pd(II) and Au(II) ions, followed by the wet-chemical removal of redundant Co atoms with an acidic solution.[97] Due to the distortion of Pd lattice, a tensile outer layer and a compressive inner layer are formed in the PdAu nano-chains.
A strengthened strain state is obtained (Figure 6f–h). The as-prepared PdAu nano-chains are strain-rich and exhibited quite lower ORR overpotential, as well as, more outstanding stability even than the benchmarked Pt/C catalyst.

The bulk defects occur in the form of voids or pores. For example, the strain has been induced in a hollow PdNi/C alloy by use of bulk defects.[98] The hollow PtNi/C alloy has both convex and concave sites, which lead to the deviation of atoms from their ideal positions. The hollow structure was changed when the PtNi/C catalyst was thermally treated in air, N₂, or H₂ atmosphere. The treated PtNi/C catalysts exhibit different X-ray diffraction (XRD) peak locations, indicating changed strain states. The obtained strains were proposed to be stemmed from their altered porous morphologies after the applied post-treatment. The treated PtNi/C catalysts showed lower ORR overpotential and better stability than other PtNi alloy catalysts.

It has to be mentioned here that the defects in the catalysts are generally introduced during the synthesis process. For example, during a chemical vapor deposition process, atom-thin transition metal dichalcogenides (MoS₂, WS₂) have been synthesized on an Au layer coated SiO₂/Si wafer, where rich grain boundaries are found.[100] Another example is copper electrodeposition on carbon paper. By use of a Cu(NO₃)₂ + poly(vinylpyrrolidone solution and a deposition potential of −0.3 V (vs Ag/AgCl), Cu nanoparticles with grain boundaries were synthesized.[101] The defects have been generated during the post-treatment of as-prepared materials. The S defects on the MoS₂

Figure 5. The mechanism of strain regulation of Pt nanoparticles in the Pt/LCO catalyst: Synthesis steps of a) tensile and b) compressive Pt nanoparticles. Reproduced with permission.[54] Copyright 2016, American Association for the Advancement of Science. c) Synthesis steps of the Pt/Ni branches. Reproduced with permission.[52] Copyright 2019, American Chemical Society. d) Synthesis steps of a strained FeP₂@C catalyst. Reproduced with permission.[55] Copyright 2020, Wiley-VCH.
catalysts have been formed via etching fresh MoS$_2$ catalysts in a H$_2$O$_2$ solution. The dissolution of vanadium, namely electrochemical treatment of as-prepared NiV layered double hydroxide nanosheets by means of cyclic voltammetry within a potential range of 0 to 0.7 V (vs Hg/HgO) leads to the generation of a $\beta$-Ni(OH)$_2$ catalyst with the tensile strain. Since the methods to prepare defect-rich catalysts have been summarized in some previous reviews, in this review only some recent advances on these methods are briefly introduced as examples.

2.1.4. Strain in Alloy

The fourth form of the strain has been found in a bimetallic alloy when a different atom (e.g., with a small atomic number) is doped into the surface of the main metal (Figure 7a). The dissolution of vanadium, namely electrochemical treatment of as-prepared NiV layered double hydroxide nanosheets by means of cyclic voltammetry within a potential range of 0 to 0.7 V (vs Hg/HgO) leads to the generation of a $\beta$-Ni(OH)$_2$ catalyst with the tensile strain. Since the methods to prepare defect-rich catalysts have been summarized in some previous reviews, in this review only some recent advances on these methods are briefly introduced as examples.

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catalyst surface. More importantly, it has to be highlighted that this alloy strategy is especially effective for these fcc metals (e.g., Cu, Ni, Pd, and Pt). For example, a series of PtM (e.g., PtNi,\textsuperscript{109} PtCo,\textsuperscript{110} and PtFe\textsuperscript{111}) and PdM (e.g., PdCo,\textsuperscript{112} PdBi\textsuperscript{113}) alloys have been designed and synthesized. As expected, their strain states are tunable or adjustable. A volcano curve has been drawn for the synthesized PtM alloys (M = Tm, Dy, Tb, Gd, Sm, Ca, Ce, or La) (Figure 7d), namely the relationship between their ORR activity and their lattice parameters.\textsuperscript{114,115}

Besides binary alloys, the lattice strain has been found in the ternary alloys. For example, the variation of lattice strain in a Pt-Pd-Cu ternary alloy has been found when the atomic ratios of Pt to Pd to Cu are adjusted (Figure 7e,f). A Pt\textsubscript{20}Pd\textsubscript{20}Cu\textsubscript{60} alloy/nanoparticle featured an optimized strain and exhibited lower ORR onset potential than other Pt\textsubscript{20}Pd\textsubscript{X}Cu\textsubscript{80-X} alloy catalysts.\textsuperscript{116}

2.1.5. Strain Induced by Size and Shape Variation

It is known that the length of a local atom-atom on the surface of a nanoparticle is different from its bulk material, originating from the nature of tending to a more stable state.\textsuperscript{118–121} Different from that a bulk atom is fully coordinated, a surface atom is in a state of coordination desaturation and thus has higher surface energy.\textsuperscript{122} The difference of chemical potential ($\mu$) between a particle with a radius of $R$ ($\mu(R)$), and bulk material ($\mu(\infty)$), can be described by the Gibbs-Thompson equation:

$$\mu(R) - \mu(\infty) = 2\gamma\Omega/R$$

where the symbol $\gamma$ and $\Omega$ correspond to the surface free energies of an atom and a bulk metal’s volume per atom (a constant), respectively. For a nanoparticle with a smaller size, it has a higher surface free energy.\textsuperscript{40,123} Based on the molecular dynamics simulations,\textsuperscript{59} a smaller particle has a higher chemical potential. To reduce this chemical potential, the surface atom tends to be compressed. In other words, a smaller particle has a more compressive lattice parameter. Taking Cu nanoparticles with different sizes as an example, the lattice parameters are significantly increased when the particle sizes are enlarged from 2 to 7 nm. However, they are inconspicuously increased when their sizes are enlarged from 7 to 14 nm. Consequently, the strain of nanomaterials is more obviously affected within a small size.

The strain in a catalyst is also affected by its shape or the exposed facets.\textsuperscript{124} This is because the coordination numbers of the surface atom are related to the shape of a catalyst. For example, the surface atoms of a nano-tetrahedron catalyst have...
lower coordination numbers than those of a nanocube catalyst. Although the Pt$_3$Ni icosahedra and octahedra particles have the same exposed (111) facets,[60] the Pt$_3$Ni icosahedral catalyst exhibited better ORR performance than the Pt$_3$Ni octahedral catalyst. This is because of different strain states in the icosahedral and octahedral catalysts (Figure 8a). Similarly, such different strain states were observed on the Pd octahedral and Pd icosahedral catalysts.[125] The Pd icosahedra catalyst shows a more negative XRD peak location than the Pd octahedral catalyst, proving the existence of a compressive strain in the Pd octahedra catalyst (Figure 8b). Such a strain has been further confirmed from the strain mapping images of the Pd octahedra and Pd icosahedral catalysts (Figure 8c–f). The compressive strain has been found to influence the properties of the Pt shell (skin) that are grown on the Pd cores with different shapes. The Pd@Pt icosahedra catalyst exhibited better ORR performance than the Pd@Pt octahedral catalyst.[72]

2.2. Strain-Rich Supports to Load Single-Atom Catalysts

Single-atom catalysts exhibit excellent performance toward different electrochemical reactions, originating from the strong interactions between single-atom sites and the support. In this context, the introduction of strain into a support can change its electronic structure and further regulate the catalytic activity of single-atom sites. For example, the strain states of single Ru atoms supported on the PtCu alloys have been adjusted by varying the atomic ratios of Pt to Cu (Figure 9a).[108] This Ru-Pt$_3$Cu electrocatalyst then displayed lower OER overpotential than the Ru-PtCu and Ru-PtCu$_3$ electrocatalysts (Figure 9b). This lowest OER energy barrier among three SREs (Figure 9c) was interpreted using an optimized d-band center of a Ru site by the strain states of the support. The strain-rich MoS$_2$ support was utilized as a propellant to prepare an atomically dispersive Ru-catalyst for the HER (Figure 9d).[126] On this electrocatalyst, the electronic structure of Ru atoms was optimized by this strain-rich MoS$_2$ substrate,[126] leading to superior HER performance (here a reduced $\Delta G_H$ value to the counterparts) (Figure 9e) of the HER. When the Fe-N$_4$ site was supported on the high-curvature and helical carbon, the compressive Fe–N bond (about 1.5%) was induced by a surface curved geometry (Figure 9e).[127] Thus the d-band center of the compressive Fe site was negative than that on the planar site, leading to the weak adsorption energy toward O* intermediate and lower energy barrier for the ORR (Figure 9f). When Rh atoms were atomically dispersed on the S-Co$_3$O$_4$ (with tensile strain 0.8–10.7%) and P-Co$_3$O$_4$ (pristine Co$_3$O$_4$ with no strain) substrates,[128] higher Rh loading was achieved on the S-Co$_3$O$_4$ (6.6 wt%) substrate than on the P-Co$_3$O$_4$ (3.1 wt%) substrate. This was because the tensile strain in Co$_3$O$_4$ led to the decrease of the formation energy barrier for a single Rh site (Figure 9g). In short, the electronic structure of single-atom sites can be modified by use of the strain-rich support. As-prepared electrocatalyst can then exhibit better performance than the single-atom site catalyst (where no strain on the support exists). Meanwhile, the strain on the support can accelerate the formation of single-atom sites, leading to higher loading of single-atom catalysts on a desirable support.

2.3. Surface Strain Analysis

2.3.1. Strain Characterization

A comprehensive characterization of a SRE is quite beneficial to analyze its lattice strain and to further evaluate its catalytic performance. The most common and direct tool to calculate the strain in a SRE is high-resolution transmission microscopy (HRTEM). From the HRTEM image of a SRE, one can directly tell the atom-atom distance(s). For example, when Pt particles are supported on different supports, different Pt-Pt atom distances have been confirmed from their HRTEM images.
Moreover, a detailed strain calculation can be quantitatively applied via the comparison of the measured atom-atom distance from the HRTEM image of a SRE with its standard material. In a case study, the Pd-Pd distances in the (111) crystal space of a Pd nanosheet were measured from its HRTEM images before (Pd NSs, Figure 10e) and after (Pd-s PNSs, Figure 10f) the application of plasma post-treatment. They are 2.20 and 2.27 Å, respectively. In addition, the lattice mismatch can be also testified by strain mapping with aid of HRTEM. For example, no obvious lattice strain is visible in the Pd NSs (Figure 10g), while the tensile lattice strain is clearly observed in the Pd-s PNSs (Figure 10h).

Despite the strain calculation method based on the HRTEM image of a SRE is simple and visual, its limitation is quite obvious. It only reflects the strain information of a local area or a specific particle. In this context, the calculation of strain state(s) of a SRE always needs other technologies such as, XRD, pair distribution function (PDF), and extended X-ray absorption fine structure (EXAFS). When the XRD is applied, the diffraction peak location can be related to the interplanar spacing between a catalyst and the wavelength of the X-ray (a constant incident). Hence, the interplanar spacing is inversely proportional to the diffraction peak location. Namely a more negative diffraction peak corresponds to a larger lattice parameter. For example, when the lattice parameter of a Pt nanoparticle is enlarged (e.g., due to the change of the support), its diffraction peak will be negatively shifted. On the contrary, when the lattice parameter of a Pt nanoparticle is decreased, a positive shift of its diffraction peak is expected. However, XRD cannot be applied to thin layers of core–shell structured catalysts, amorphous materials, and nanoclusters. This is because those materials are not ordered in a long range. Differently, the atomic PDF method is based on the high energy X-ray scattering and thus more powerful to measure lattice parameters and order degrees of different catalysts in both long and short ranges. For example, the lattice parameters of a series of

**Figure 9.** a) HAADF-STEM image of a Ru1-Pt3Cu catalyst. b) OER polarization curves of the Ru1-Pt3Cu and the contrast catalysts. c) The volcano curve of OER activity on the Ru-PtCu alloy catalysts. Reproduced with permission. Copyright 2019, American Chemical Society. d) Illustration of the construction of Ru/nP-MoS2. e) Free energy diagrams for HER at different sites. Reproduced with permission. Copyright 2021, Springer Nature. f) EXAFS fitting results of D-Fe SAC and LD-Fe SAC. g) ORR LSVs of D-Fe SAC and contrast samples. Reproduced with permission. Copyright 2021, Wiley-VCH. h) The energy barriers of the migrating of Rh atom on S-Co3O4 and P-Co3O4. Reproduced with permission.
Pt$_x$Fe$_{100-x}$ nanowires have been determined by use of the PDF crystallography-constrained simulations (Figure 10i). The lattice parameters of the Pt$_x$Fe$_{100-x}$ catalysts decrease from 3.918 to 3.839 Å with an increase of the Fe content from 0 to 0.88. Moreover, the difference in the order degree of those catalysts has been well explained by the PDF. The Pt$_{42}$Fe$_{58}$ catalyst was detected to be ordered in a short range but disordered in a long range.

Since the strain can be formed under various conditions by means of different mechanisms, the precise measurements of strain states of a SRE by means of individual strain characterization techniques are somehow difficult. In this regard, the integration of multiple strain characterization methods is of great significance to achieve more precise and deeper analysis of the stain(s) of a SRE. Such a combination is thus expected to make the strain detection of a SRE easier and more reasonable. For example, the Fourier transform and wavelet transform results of the EXAFS spectra have been frequently combined with HRTEM images to calculate the strain(s) of a SRE. This combination reflects more deeply the coordination environment and the coordination bond length of a SRE. For example, the strain in the IrO$_x$ layer of this CoIr@IrO$_y$ catalyst has been identified using this method (Figure 10j), where an increase of the Ir–O bond distance via the addition of layer number of the shell weakens the strain intensity in this core–shell structured catalyst (Figure 10k). In another example, the lattice parameters of a series of PtNi alloys were measured by means of XRD in the first step, confirming a decrease of...
their lattice parameters as an increase of Ni atoms in the PtNi alloy. Subsequently, the coordination environment in the first shell was measured by means of the EXAFS and corresponding wavelet transform. The formation rates of the Pt–Ni bond were testified to be increased with an increase of Ni atoms in the PtNi alloy. The Pt–Pt bond length remained stable, while the Pt–Ni bond length became obviously short. To get long range coordination information of the PtNi alloys, PDF was further carried out, by which the disordered fcc structure of a Ni-atom rich PtNi alloy was confirmed.[142]

2.3.2. Mathematic Simulation of Surface Strain

The theoretical calculations by means of molecular dynamics (MD) methods have been employed to simulate the strain states of SREs. This is because integration of these MD simulations with the results from other characterization techniques will get deeper insight into the strain states of SREs. For example, MD analysis of Al nanoparticles with different sizes[59] confirmed their varied lattice parameters, namely the strain formation in these nanoparticles. The Al nanoparticle with a smaller size (e.g., 2 nm) had a smaller lattice parameter than those with larger sizes (e.g., 5, 8, 10, and 15 nm). This result was in line with the strain formation mechanism, calculating according to the Gibbs-Thompson equation.

Moreover, the MD methods were extended to simulate the variation of surface strain of SREs with their shape and defects. By means of the MD methods, the strain mappings of later-transition metals and alloy nanoparticles owning high-index facets have been studied.[143] The strain states in the surfaces of different nanoparticles were revealed to be different, although their high-index facets were same. For example, the compress strain of Pt, Pd, and Au nanoparticles was observed on the surface step and kink atoms, while no obvious strain was observed in their terrace atoms (Figure 11a–c). Differently, the tensile strain of Cu, Ni, and Ag nanoparticles was clearly observed in their terrace atoms (Figure 11d–f). Consequently, the element type affects the surface strain states in a defect-rich nanoparticle and thus determines the reaction mechanisms of different SREs toward different reactions.

In addition to defect-rich nanoparticles, the MD methods have been proved to be useful for the strain analysis of SREs with a core–shell structure. For example, although the Pt shell was proved to be compressive in the PtCu@Pt core–shell structure, the difference of the strain distribution on these nanoparticles was unclear, especially when the sizes of PtCu@Pt nanoparticles were varied. With aid of the MD methods, the detailed strain information of different PtCu@Pt nanoparticles with different Cu/Pt ratios, sizes, shape was elaborated.[86] For a CuPt-alloy core that is coated with a Pt shell with a constant size and tunable Cu/Pt atom rates, the MD simulations revealed that the compressive strain intensity on the Pt shell was reduced with a decrease of Cu amount (Figure 11g). The strain state of the Pt shell was also found to be affected by the size of the PdCu-alloy core. When the amount of Pt atoms is higher than that of Cu atoms in the PtCu-alloy core, the compressive strain of the Pt shell is increased with a decrease of the core size. On the contrary, the compressive strain of the Pt shell is decreased with the decrease of the core size when there is a smaller amount of Pt atoms than Cu atoms in the PtCu-alloy core. In addition, the MD simulations proved that the strain distribution was different when the compressive strain of Pt shell was intense. For example, the layer thickness of a Pt shell that is coated on a Pd_{30}Cu_{70}-alloy core affected the compressive strain of the Pt shell. This compressive strain of the Pt shell when its thickness was 3 Pt atomic layers was heavier than that when its thickness was 5 Pt atomic layers. Namely, the strain intensity in the Pt shell was decreased with an increase of the thickness of Pt atomic layers. However, the compressive strain of the Pt shell when its thickness was 3 Pt atomic layers was more uneven than

![Figure 11. The surface strain distributions on the (322) facet of metal nanoparticles. a) Pt-322, b) Pd-322, c) Au-322, d) Cu-322, e) Ni-322, f) Fe-322. Reproduced with permission.[143] Copyright 2021, Wiley-VCH. g) Strain changes of Pt shell coated on PdCu alloy nanoparticles with different sizes and Pd Cu atom rate. Surface strain distribution of Pt shell with different layers coated on PdCu alloy nanoparticle. h) 3 layers, i) 5 layers. Reproduced with permission.[86] Copyright 2015, American Chemical Society.](https://www.advancedsciencenews.com)
that of the Pt shell when its thickness was 5 Pt atomic layers. Such results were explained by that high stresses of the Pt shell are relaxed by nucleation of dislocations (Figure 11h,i). The strain state of Pt shell was also affected by the shape of a CuPt core. When the PdCu-alloy core was in the form of nanorod, a stronger compressive strain of the Pt shell was found in the upper and lower surfaces of the nanorod.[66]

2.4. The Stability of Strain-Rich Electrocatalyst

The stability performance of a catalyst is another crucial issue to evaluate its various electrochemical applications. During the electrochemical processes, the atoms are possible to dissolve from a catalyst surface, leading to its structure change and eventually its catalytic performance decrease. For an electrocatalyst with a core–shell structure, its stability is thus highly dependent on the interaction between the shell and the core. A stable metal core always stabilizes diffluent shells. For example, an underlayer Au core improved the stability of low-coordinated Pt sites and prevented its dissolution during the ORR.[144,145] This strategy has been applied to other electrocatalysts. For instance, the Au@Pt[66] and Au@PdPt[146] electrocatalysts exhibited better stability than the Pt/C electrocatalyst toward the ORR and the MOR. Meanwhile, an electrocatalyst with a core–shell structure remains its stability via the optimization of its size, even when a metal core is not stable enough in the electrolyte. Take the Pd@Pt nanoparticles as example, their investigation by means of liquid cell transmission electron microscopy[147] reveals that the inner Pd core (with a size of 8 nm) in an octahedra Pd@Pt electrocatalyst is first dissolved and eventually formed a Pt nanocage. Such a process was slower than those featuring an inner Pd core (with a size of 37 nm) in an octahedra Pd@Pt electrocatalyst (Figure 12a). This was explained with a tensile strain state optimization of an octahedra Pd@Pt electrocatalyst via its size regulation. However, further prevent of the dissolution of a Pd core is still desirable in the Pd@Pt catalyst. In another case, the Ir atoms that were introduced into the Pt skin surface or into the interface between Pd and Pt atoms enhanced the stability of a Pd@Ir@Pt or Pd@Pt@Ir electrocatalyst.[148] Both Pd@Ir@Pt and Pd@Pt@Ir electrocatalysts exhibited higher stability during the ORR stability than the Pd@Pt catalyst (Figure 12b). The strong interactions among the metal atoms were suggested to be main reason behind. The introduction of WNi into a Pd@Pt electrocatalyst led to the formation of a stable WNi@Pd@Pt structure,[149] which displayed quite obvious enhancement in the stability performance of a Pd@Pt electrocatalyst toward the ORR (Figure 12c) when compared with the Pd@Pt electrocatalyst.

The design and optimization of the interactions between a metal electrocatalyst (metal atoms) and the support have been utilized to improve the stability of electrocatalysts. For example, to reduce the dissolution of Pt atoms for the Pt/C electrocatalysts, SnO2 nanotubes were proposed to substitute the carbon...
support to load Pt nanoparticles, stemming from strong interactions between Pt atoms and SnO₂ nanotubes. The resultant Pt/SnO₂ electrocatalysts thus featured better stability than the Pt/C electrocatalyst during the ORR.

In terms of alloy electrocatalysts, there exist two main strategies that have been utilized to enhance their stabilities, namely their atom modification and reconstitution of their surface structures. For example, the dissolution of Pt and Ni in PtNi alloy was hindered in the electrolyte when Mo atoms are introduced onto the surface of a PtNi alloy (Mo-PtNi). In this case, the surface Pt atoms are coordinated with the neighbor Mo atoms, leading to the formation of stable metallic bonds. Similarly, Au atoms stabilized the Pt sites in Pt₃Ni-alloy nanowires. With respect to reconstitution of surface structures of alloy electrocatalysts, the structure of a PtM (or PdM) alloy was found to be transformed to a PtM@Pt structure during the ORR, resulting in newly available and stable electrocatalytic surface and eventually better stability of a PtM@Pt electrocatalyst than the PtM alloy.

A defect-rich catalyst always contains different kinds of defect sites (e.g., high-angle grain boundary sites, low-angle grain boundary sites, and atomic steps on the assemblies surface) which own varied strain states and coordinate numbers. During a thermally catalyzed graphitic layer growth model, the reconstitution of these different defect sites might occur. High-angle grain boundaries probably become smooth, while edge boundaries and low-angle grain boundaries perhaps turn to be rough. The stability study of defect-rich Ag nanoparticles during cyclic voltammetric tests proved that the dissolution of Ag atoms occurred during the positive scan while the redeposition of Ag atoms took place during the negative scan. Both the defect sites and strain sites exhibited higher dissolution kinetics.

2.5. Strain Theories

To design high-performance SREs for different electrochemical reactions, knowing the reaction mechanism and strain regulation ruler are both important. In the past few years, progress in theory such as, the d-band center theory, electrochemical reaction free energy barrier calculation method, and scaling relations make the electrocatalyst design be easier. In this section, we will first discuss the basic strain regulation mechanism. Then, the scaling relation in electrochemical reactions is introduced and discussed. Finally, some progress of breaking the scaling relation by strain is summarized.
2.5.1. Basic of Strain-Adsorption-Catalyze

It has been widely accepted that the intrinsic activity of a catalytic site is highly relevant to its adsorption energy toward the reactant(s), relative intermediate(s), and product(s). According to the Sabatier principle, the adjustment or optimization of the adsorption ability of a catalytic site during the catalyst design is thus crucial. When a species is adsorbed on a metal active site, their electrons interact with each other, resulting in the formation of new bonding and anti-bonding orbitals (Figure 13a).\textsuperscript{[155–157]} The anti-bonding orbital has a close energy to the Fermi level and then is partially occupied.\textsuperscript{[158]} The anti-bonding orbital with a higher energy than the Fermi level indicates that more anti-bonding orbitals are empty and the adsorption of the species is more stable, which is actually due to a higher energy of a d-band center of a metal active site. In other words, the d-center of a metal site is a key index, which determines the adsorption ability of a metal active site. For example, the anti-bonding orbital locations of adsorbed hydrogen atoms on Ni (111) and Pt (111) metal sites are higher than that of Fermi Level (no electron in anti-bonding orbitals), while anti-bonding orbital locations of adsorbed hydrogen atoms on Au (111) and Cu (111) metal sites (electron fully occupied in anti-bonding orbitals) are lower than that of Fermi Level (Figure 13b). Therefore, the adsorption energies of hydrogen atoms on Ni (111) and Pt (111) metal sites are higher than those on Cu (111) and Au (111) metal sites, derived from the fact that the energies of d-band centers of Ni (111) and Pt (111) metal sites are higher than those of the d-band centers of Cu (111) and Au (111) metal sites.\textsuperscript{[154]} Moreover, the adsorption energy of an adsorbate always can be linearly fitted with the energy of the d-band center of a metal site (e.g., the adsorption of O species on transition metal surface) (Figure 13c,d).\textsuperscript{[128]} Hence, tuning the d-center structure of a metal site on a catalyst is also a useful method to adjust the adsorption energy of reactant(s), intermediate(s), and product(s) during different electrocatalytic reactions.

The d-center electron structure/state of a transition metal atom is affected by its coordination environment (e.g., type of coordination atoms, coordination numbers, and bond length of the coordination). In this context, strain engineering of an electrocatalyst has been frequently carried out in the past years to regulate the electronic structure of a catalyst. The change of bond length of coordination of metal sites on an electrocatalyst is one of the main approaches.\textsuperscript{[159]} Taking the most common Pt (111) catalyst as a model, the average coordination distance of a Pt–Pt bond on the Pt surface is increased when the lattice parameter of the Pt catalyst is increased (e.g., resulting from the tensile strain). The change of the coordination degree that is caused by tensile strain further makes the d-electron bandwidth of Pt atoms decreased. The energy of a d-band electron of Pt atoms shifts to the Fermi level, namely a d-band center of a Pt atom with a higher energy.\textsuperscript{[156]} On the contrary, the compressive strain results in a d-band center of a Pt atom with a lower energy (Figure 13e). Such an approach of regulating the d-band center of a metal site on a catalyst has been extended to other transition metals (e.g., Pd, Rh, Ni, and Cu). For example, the adsorption energies of ORR intermediates (e.g., O*, OH*, OOH*) were varied on different strain states of a Pt (111) surface. This is because a tensile strain increases the adsorption energies of these intermediates, while a compressive strain reduces their adsorption energies. Since a tensile or compressive strain is linearly fitted with the energy of d-band center of the Pt (111) facet, these binding energies of different ORR intermediates (e.g., \( \Delta G_{O} \), \( \Delta G_{OH} \), and \( \Delta G_{OOH} \)) change accordingly (Figure 13f).\textsuperscript{[34]} An ideal adsorption state is thus expected to be achieved by adjusting the surface strain state of a SRE.

Theoretical calculations seem to be efficient for the interpretation of the strain effect of a SRE. However, in the practical systems, other effects need to take into consideration. Note that some inconsistent experimental results with theoretical predictions have been reported for the core–shell structured catalysts. For example, although a compressive strain of a Pd catalyst was proposed to be beneficial for the ORR, a tensile Pd shell in a Pd/Pb-core-Pd-shell catalyst showed better ORR performance.\textsuperscript{[160]} The onset and half-wave potentials of this Pd/Pb/Pd catalyst toward the ORR were more positive than those of the Pd/C and Pt/C catalysts. The excellent ORR performance of the Pd/Pb/Pd catalyst was rationalized only after taking both ligand and strain effects into consideration.

2.5.2. Breaking Scaling Relation by Strain

The recently designed HER electrocatalysts exhibited only a low overpotential toward the HER (e.g., 5 mV for a PtNi@Pt SRE in acidic solution).\textsuperscript{[165]} However, the design of advanced SREs with low overpotential toward the OER and ORR is still difficult. This is because multi-intermediates exist during the ORR and OER. Since the interaction between these intermediates and active sites of an electrocatalyst (e.g., metallic atoms) occurs on the same site, the binding energies of \( \Delta G_{O} \), \( \Delta G_{OH} \), and \( \Delta G_{OOH} \) are possible to be linearly fitted for different kinds of active sites on the metal catalysts (Figure 14a).\textsuperscript{[162]} The relations of \( \Delta G_{O} \), \( \Delta G_{OH} \), and \( \Delta G_{OOH} \) can be expressed as follows:

\[
\Delta G_{OOH} = \Delta G_{OH} + 3.2
\]

\[
\Delta G_{O} = 2\Delta G_{OH}
\]

The coefficient in Equation (4) is 2. This is because the adsorption of OH* on a metal active site leads to the formation of a double bond (namely, an O=M bond). Differently, the adsorption of O* and OOH* on a metal active site only results in the formation of a single bond (namely, an O–M bond), which is called linear scaling relation. Based on this scaling relation, the ORR rate-limiting step has been simply expressed (Figure 14b). The binding energy of OH* is thus a good descriptor for the OER. When the adsorption of OH* is too strong, the ORR activity is limited by the process of \( \text{OH}^* \rightarrow \text{H}_{2}\text{O} \). On the contrary, when the adsorption of OH* is too weak, the ORR performance is limited by the process of \( \text{O}_{2} \rightarrow \text{OOH}^* \). Theoretically, the best reaction potential for the ORR has been revealed to be about 0.86 V (vs RHE) at the top position in the ORR volcano curve. In comparison to the ORR, the OER involves the same intermediates but different reaction order. In other words, the OER overpotential is also limited by the scaling relation. The theoretical minimum overpotential of the OER was estimated to be about 0.37 eV on the metal surface.
The scaling relation between $\Delta G_{\text{OOH}}$, $\Delta G_{\text{OH}}$, and $\Delta G_{\text{O}}$ is slightly different on the surface of some electrocatalysts (e.g., ABO$_3$ oxides, metal oxides). The theoretical minimum overpotential of the OER on the surfaces of ABO$_3$ oxides and metal oxides are about 0.33 and 0.26 eV, respectively.[163,164] Similar tendency has also been found for the NRR and ECO$_2$RR, where the binding energies of CO$_\ast$ and N$_\ast$ are the descriptors of the activity of the ECO$_2$RR and NRR, respectively.

Based on the scaling relation, the SREs can be designed more efficiently. However, the unavoidable overpotential makes the design of the ideal SREs difficult. Breaking the scaling relation is thus of great importance. The introduction of $p$ states into a SRE, the addition of a second adsorption site and/or a proton acceptor group, surface lattice strain, and the changes of solvent composition are useful methods to break the scaling relation.[165] Note that the breaking scaling relation by use of lattice strain has not been elaborated in detail. On the N-doped graphene surface, the scaling relation of the ORR is broken because both tensile strain and adsorbed O$_\ast$ atom can strengthen the N–C$_\ast$ bond. The breaking of the scaling relation occurred when the electrocatalyst was tailored to be selectively in resonance with the adsorption of the intermediates.[166] The lattice strain cannot break the scaling relation for the ORR on the Pt (111) surface. In this case, the binding energies of three

Figure 14. a) The linear relations of binding energies of OOH$_\ast$ and O$_\ast$ ($y$-axle) toward OH$_\ast$ ($x$-axle). b) The volcano plot of ORR on the metal surface. Reproduced with permission.[162] Copyright 2018, American Chemical Society. c) The binding energies of O$_\ast$, OH$_\ast$, and OOH$_\ast$ on different strain Pt (111). d) The binding energies of O$_\ast$, OH$_\ast$, and OOH$_\ast$ on different layers Pt (111) coated on CrC (111). Reproduced with permission.[167] Copyright 2017, Wiley-VCH. e) The binding energy change of COOH$_\ast$, CO$_\ast$, CHO$_\ast$, and COH$_\ast$ with different strain states on Cu (211) and Cu (100) surfaces. Reproduced with permission.[169] Copyright 2021, American Chemical Society. f) Determination of the sign of eigenstress. g) Applying uniaxial compression to the surface and the qualitative picture of energy level changes of the IS and TS. Self-diffusion of Pt atoms on Pt (100) surface. h) Schematic of inline diffusion and transverse diffusion. i) The energy barriers of inline diffusion on different strained Pt(100). j) The energy barriers of transverse diffusion on different strained Pt(100). Reproduced with permission.[170] Copyright 2018, Springer Nature.
intermediates (namely, O*, OH*, OOH*) were linearly changed with the tuning of the strain states (Figures 13f and 14c).[54] For an electrocatalyst with a core–shell structure, it can break the scaling relation when the Pt shell consisted of only one atomic layer.[167] The adsorbed O* is on the hollow site while the adsorbed OH* and OOH* are on the top site. In other words, the adsorption of O* on the hollow site is affected stronger by the atoms in the second layer of the core than the adsorption of OH* and OOH* on the top site. In this respect, the binding energy of O* was effectively regulated while the binding energies of OH* and OOH* did not obviously change when the layer number of the shell was changed (Figure 14d). Namely, the scaling relation can be broken based on the ligand effect in a core–shell structured catalyst. This method has also been applied for the OER. However, the breaking of scaling relations of the ORR/OER is challenging, due to the close adsorption bond types of three intermediates (O–M bonds).

As for other kinds of electrochemical reactions such as ECO2RR, breaking the scaling relations is easier than ORR by lattice strain.[168] For example, the adsorption energies of COOH* and CHO* intermediates during the ECO2RR on Cu(100) and Cu (211) surface increase, while those of CO* and CHO* intermediates decrease with the improvement of uniaxial tensile strain (Figure 14e).[169] This opposite response of adsorption energies is a sign of breaking the scaling relation of the ECO2RR. The essential reason was attributed to the different types of adsorbate-induced strains. Another strain-adsorption investigation well confirmed such an adsorbate-caused strain.[169] When the CH2 is adsorbed on the bridge site of Cu (110), the neighboring two Cu atoms are pushed outward, resulting in a compressive strain in the region adjacent to adsorbed CH2* (Figure 14f). The lattice strain thus resulted in opposite change of related adsorption energies. The anisotropic strain has also been applied to break the scaling relations. When the lattice is compressive along with the y-axis, the lattice along the y-axis is tensile accordingly. They are attributed to the effect of the Poisson response (Figure 14g). The adsorption energy of the intermediate of initial state (IS) at fourfold site decreases, affected by both compressive strain along the x-axis and tensile strain along the y-axis. Differently, the adsorption energy of the intermediate of transition state (TS) at the bridge sites increases, just affected by the tensile strain along the y-axis (Figure 14g). The theory was also verified by surface migration reaction of a Pt atom. The compressive strain along the x-axis of Pt (100) reduced the energy barrier of surface diffusion of Pt atoms along the x-axis. However, it did not decrease the energy barrier of surface diffusion of Pt atoms along the y-axis (Figure 14h–j). In other words, the scaling relation of IS and TS along the x-axis was broken.

3. Applications of the Electro catalysts with Strain

Since the electronic structure of an electrocatalyst can be regulated by its lattice strains, numerous electrocatalysts based on the strain effect, namely, SREs have been designed, synthesized, characterized, and further explored for diverse electrocatalytic applications. In this section, the applications of different SREs for several typical electrochemical reactions are summarized, mainly including ORR, HER, OER, AOR, ECO2RR, and NRR.

3.1. Oxygen Reduction Reaction

As one of the main cathodic reactions, the ORR plays important role in fuel cells and metal-air batteries. In order to obtain high efficiency in these energy conversion devices, a 4-electron transfer reaction is always pursued. However, this multi-electron transfer reaction inevitably has sluggish reaction kinetic. For the dissociative mechanism of ORR, adsorbed O2* dissolute to two O*, followed by transforming to OH* and H2O in acid or OH– in alkaline. As for the associative mechanism of ORR, three intermediates appear in sequence (OOH*, O*, OH*). In general, the ORR catalyst design is based on scaling relations. The binding energy of OH* which described the activity of ORR can be regulated by lattice strain.

Pt-based (and Pd-based) nanomaterials are potential ORR catalysts due to their relative suitable ΔGOH value. For the Pt-based ORR catalyst designing, the compressive strain is beneficial to reduce their adsorption nature and get the most suitable binding energy of intermediates. In some theory prediction investigations, core–shell structure catalysts with compressive Pt skin are expected to have better ORR performance than Pt. The ORR performance of a Pt skin coated on Cu40.76Ni0.24 alloy (158 atoms) with an icosahedral shape and a small size Pt nanoparticle (3 nm) is investigated by density-functional theory (DFT).[171] Due to the compressive strain in CuNi@Pt and optimized d-band center of surface Pt skin (Figure 15a,b), the CuNi@Pt exhibited lower ORR overpotential (0.35 eV) than Pt(111) (0.48 eV).

Many kinds of core–shell structured nanomaterials have been designed (with optimized strain states), synthesized, and utilized as the SREs for the ORR in both acidic and alkaline media (Table 1).[10,44,49,72,78,84,93,109,113,153,160,172–188] Clearly, the lattice strain of an electrocatalyst displays an effective role in its ORR performance. Most of SREs have both low onset potential and half-wave potential as well as high mass activity for the ORR. This is in line with the theoretical prediction that a compressive strain is always beneficial for the ORR on the Pt- and Pd-based catalysts, including the M@Pt and M@Pd core–shell structured catalysts as well as the PtM and PdM alloys (where M has a smaller lattice parameter or a smaller atom size than Pt and Pd). Note that the PtM and PdM alloys always have long-term stability during the ORR, resulting from the dissolution of M atoms and the reconstruction from PtM to PtM@Pt or PdM to PdM@Pd.

The ORR performance of the Pd@Pt core–shell structured catalysts is varied once the shape and the thickness of the compressive Pt skin are changed. For example, the Pd@Pt core–shell nanoparticle in the first four cases in Table 1 were synthesized using different methods. All of them exhibited good ORR performances (e.g., lower onset potential and half-wave potential than the Pt/C catalyst). In the case of the Pd@Pt core–shell nanoparticle (Figure 15c)[173] a Pd nanocube was synthesized, followed by a surface phosphorization process. This Pt nanocube
with a P-dopped surface was formed and selected as the core to add a Pt skin. The layer number of the Pt skin was controlled to be 2 and 8. These SREs were named as Pd@PtPd@PtPd@Pt8L and Pd@PtPd@Pt8L, respectively. The Pd@PtPd@Pt2L catalyst showed lower ORR onset potential and half-wave potential (Figure 15d) as well as better stability (Figure 15e) than the Pd@PtPd@Pt8L, Pd@Pt2L, and Pd@Pt8L catalysts. The mass activity of the Pd@PtPd@Pt2L catalyst only decreased 7.2% after 50,000 cycles of an accelerated deterioration test, which was much lower than that of the Pd@Pt2L and Pt/C catalysts (Figure 15f). In addition to the Pd core, the PtM-alloy core (where the M represents a metal with a smaller atom size than Pt, such as, Cu, Co, Fe, and Ni) was proved to be a good choice to be coated with a Pt skin. As expected, a compressive Pt skin was achieved because these PtM cores have smaller lattice parameters than a Pt core. The N-dopped PtCuN core–shell structured catalysts have been synthesized and employed for the ORR (Figure 15g).

The second kind of SREs toward the ORR is Pt- and Pd-based alloys (Table 1). The PtCo-alloys have been synthesized on the Co-N-C support for the ORR. The Co atoms coupled with Pt atoms were found to be beneficial for the ORR, stemming from their strain and ligand effects. Notice that both an ordered PtCo alloy and a disordered PtCo2 alloy had better ORR performance than the Pt/C catalyst (Figure 16a). Moreover, an ordered PtCo alloy had outstanding ORR stability during the progression test when a compressive PtCo@Pt electrocatalyst with a two-layer of Pt shell (skin) was utilized (Figure 16b). In the case of extremely thin PtNiRh alloy nanowires (Figure 16c), the lattice parameter of a Pt–Pt bond in the PtNiRh catalyst (2.71 Å) is smaller than that in a Pt foil (2.76 Å), a Pt/C catalyst (2.76 Å), Pt NWs (2.75 Å), and PtNi NWs (2.73 Å), as measured by means of Cu atoms be suppressive during the ORR process. A core–shell structured PtNiN@PtNi catalyst has been synthesized via N-doping of a PtNi intermetallic alloy, where the resultant stretching of the shell was caused by the doping of the N atoms in the core. This catalyst exhibited both lower ORR overpotential and higher mass activity, as well as, specific activity than the counterparts. Note that both combinative ligand and strain effects were assumed to contribute to such superior ORR performance of these catalysts.

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of EXAFS (Figure 16d). The change of the lattice parameters of the Pt-Pt bond in these catalysts results from a smaller size of Rh or Ni atom than that of Pt atom. The formed compressive strain makes the PtNiRh nanowires exhibit lower ORR onset potential than the PtNi catalyst, Pt nanowires, and the Pt/C catalyst (Figure 16e). A Pt3PdNi octahedral nanocage has been synthesized through epitaxial growth of a Pt layer on the Pd octahedral, subsequent removal of the Pd core atom via acidic treatment, and further thermal treatment under H2/Ar atmosphere with Ni(I) ions.[186] The Pt-Pt bond length in this catalyst is compressive about 0.74% than that in a Pt 3Pd nanocage. This was assigned to the doping effect of a small amount of Ni atoms. As a SRE, this Pt3PdNi nanocage exhibited more positive ORR potential than the Pt 3Pd and Pt/C catalysts, an indication of a positive effect of compressive strain in the ORR on this SRE.

In addition to the core–shell structured catalysts and alloys, 2D metallenes have been applied as the SREs for the ORR (Table 1). In a graphene-like Mo-dopped Pd bimetallene that features a curved surface, the existence of strain was confirmed (Figure 16f).[187] In 0.1 m KOH, this catalyst exhibited lower onset potential, better mass activity, and longer-term stability toward the ORR than the benchmark catalysts (Figure 16g). The key reason for this excellent ORR performance was attributed to the optimized adsorption energy of the O* intermediate (ΔG), which was caused by the strain effect, alloy effect, and quantum size effect in the PdMo bimetallene catalyst (Figure 16h).

| Catalyst                  | Electrolyte | Onset potential (V vs RHE) | Half-wave potential (V vs RHE) | Mass activity (A mgmetal–1) @–0.9 V | Ref. |
|--------------------------|-------------|-----------------------------|--------------------------------|--------------------------------------|------|
| 1 Pd@Pt TOhs             | 0.1 m KOH   | 1.07                        | 0.916                          | 1.63                                 | [49] |
| 2 Pd@Pt icosahedra       | 0.1 m HClO4 | 1.02                        | 0.95                           | 3.49                                 | [72] |
| 3 Pd@Pt octahedra        | 0.1 m HClO4 | 0.99                        | 0.94                           | 1.05                                 | [84] |
| 4 Pd@PtPd                | 0.1 m HClO4 | 0.98                        | 0.92                           | 0.54                                 | [172]|
| 5 Pd@a-Pd-Pt@Pt          | 0.1 m HClO4 | 0.99                        | 0.96                           | 1.29                                 | [173]|
| 6 PtCo@Pt                | 0.1 m HClO4 | 0.96                        | 0.93                           | 2.82                                 | [174]|
| 7 L17FePt@Pt             | 0.1 m HClO4 | 1.01                        | 0.95                           | 0.7                                  | [175]|
| 8 PtCoN                  | 0.1 m HClO4 | 0.98                        | 0.92                           | 1.15                                 | [176]|
| 9 PtNi-BNCs/C            | 0.1 m HClO4 | 1.01                        | 0.95                           | 3.52                                 | [44] |
| 10 Pt-Ni@Pt3C           | 0.1 m HClO4 | 0.93                        | 0.83                           | X                                    | [177]|
| 11 PtNiN@PtNi           | 0.1 m HClO4 | 0.98                        | 0.94                           | 1.83                                 | [178]|
| 12 PdCu@Pt              | 0.1 m HClO4 | 0.97                        | 0.93                           | 0.603                                | [179]|
| 13 L17CoNi@Pt           | 0.1 m HClO4 | 1.05                        | 0.96                           | 3.1                                  | [78] |
| 14 Pd2-Fe @Pt           | 0.1 m HClO4 | 0.88                        | 0.97                           | 2.7                                  | [180]|
| 15 Pd/PdCu@Pt NWs       | 0.1 m HClO4 | 1.01                        | 0.93                           | 1.54                                 | [181]|
| 16 Mn@Pt                | 0.1 m HClO4 | 1.01                        | 0.96                           | 1.19                                 | [182]|
| 17 C-Cu@Pd              | 0.1 m HClO4 | 0.95                        | 0.85                           | 0.39                                 | [183]|
| 18 Pd@Pb@Pd             | 0.1 m KOH   | 0.99                        | 0.92                           | 0.59                                 | [160]|
| 19 Pd@Ni/C              | 0.1 m KOH   | 0.92                        | 0.86                           | 2.2                                  | [184]|
| 20 A-M5-Pt3N@Ni         | 0.1 m HClO4 | 0.98                        | 0.92                           | 1.89                                 | [109]|
| 21 D-PtCu3/C            | 0.1 m HClO4 | 1.0                         | 0.91                           | X                                    | [185]|
| 22 PtCo/Zn11Co          | 0.1 m HClO4 | 1.01                        | 0.96                           | X                                    | [153]|
| 23 PdBi-8h               | 0.1 m KOH   | 1.0                         | 0.89                           | 0.17                                 | [113]|
| 24 PtNiRh               | 0.1 m HClO4 | 1.0                         | 0.97                           | 2.88                                 | [10] |
| 25 Pt3PdNi              | 0.1 m HClO4 | 1.0                         | 0.89                           | 1.2                                  | [186]|
| 26 PdMo bimetallene      | 0.1 m KOH   | 0.99                        | 0.95                           | 16.37                                | [187]|
| 27 Pd NSs 5ML/C         | 0.1 m KOH   | 0.98                        | 0.96                           | X                                    | [188]|
| 28 Pd metallene/C       | 0.1 m KOH   | 1.02                        | 0.90                           | 0.8                                  | [93] |

### 3.2. Hydrogen Evolution Reaction

By use of available electric energy, earth-rich water can be electrochemically converted into energy stored chemicals (e.g., hydrogen, hydrogen peroxide). The HER, the cathodic half-reaction of water splitting, occurs at a cathode and thus has been proved to be a potential electrochemical energy conversion technology to produce green hydrogen.[189] The HER mechanisms in acidic media are different from those in alkaline ones. The HER in acidic solutions begins at the formation of H* from the cleavage of the hydrogen bond from H3O+. The H2 is formed in the following step by coupling an H* to another H* or H+ in the solution, which are corresponding to
the Tafel reaction pathway and the Heyrovsky reaction pathway. Once such a HER mechanism is known, the rate-determining step during the HER can be identified according to the related Tafel slope. The volcano plot, namely the variation of adsorption energy of hydrogen ($\Delta G_H$) as a function of reaction coordinates has been widely accepted to describe the performance of an electrocatalyst for the HER. The $\Delta G_H$ value is thus a crucial descriptor for the HER activity of an electrocatalyst. The best HER performance of an electrocatalyst is believed to appear when the $\Delta G_H$ value approaches 0 eV. This is because the weak adsorption ability of an electrocatalyst restrains the formation of $\text{H}^*$, while the strong adsorption ability of an electrocatalyst may result in difficult desorption of $\text{H}^*$ (Figure 17a). According to the $\Delta G_H$ values shown in the volcano plot of the HER on most common metal catalysts (e.g., Pd, Pt, Au, Ni), the metal Pt catalyst sitting at the top of the volcano plot is the best HER electrocatalyst (Figure 17b). Although the $\Delta G_H$ value on a Pt-based electrocatalyst is superior to other metal catalysts, this value is still lower than the best theoretical value (0 eV). Namely, the adsorption of H atoms is slightly over-strengthened.

Based on the volcano plot and strain regulation principle, a compressive strain is expected to enhance the HER performance of Pt. Hence, different Pt SREs have been designed and synthesized (Table 2). For example, the Ru@Pt nanoparticle (Figure 17c) has a compressive Pt shell (skin) (Figure 17d), due to a smaller lattice parameter of Ru than that of Pt. This SRE exhibited superior HER performance than a pure Pt foil and a RuPt alloy in both acidic and alkaline solutions. Due to the existence of a compressive strain effect, the suitable $\Delta G_H$ of the Ru@Pt catalyst was found. The PtNi@Pt nanowires have been loaded on a WO$_X$ support, where the Pt layers on the shell were found compressive. This WO$_X$-PtNi@Pt SRE displayed lower HER overpotential than the contrast PtNi NWs and Pt/C catalysts in acidic, neutral, and alkaline media. Theoretical calculations confirmed low HER energy barriers of the WO$_X$-PtNi@Pt SRE in both acidic and alkaline media. A Pd-core and a Pt-shell nanocrystal SRE (Pd@Pt) has been synthesized, generating a compressive strain on Pt skin. For comparison, the lattice parameter of a Pd core is enlarged by hydrogenating (PdH@Pt), namely the compressive strain in Pt skin is weaker. On this Pd@Pt catalyst, the Pt shell exhibits an optimized electronic structure, which is suitable for hydrogen adsorption. The ligand effect was also adjusted via varying the layer number of the Pt shell. The Pd@Pt$_x$ catalyst showed superior HER performance

Figure 16. a) ORR polarization curves of the Pt/Vulcan, PtCo$_2$/Zn$_6$Co, and PtCo/Zn$_{11}$Co catalysts. b) HAADF-STEM image and corresponding element mapping of a PtCo catalyst before and after 20,000 cycles. Reproduced with permission. Copyright 2020, American Chemical Society. c) TEM image of the PtNiRh NWs. d) EXAFS spectra and e) ORR polarization curves of the PtNiRh NWs and contrast catalysts. Reproduced with permission. Copyright 2018, American Chemical Society. f) HAADF-STEM image of a PdMo bimetallene. g) ORR polarization curves of the PdMo bimetallene and counterpart catalysts. h) Adsorption energies of O atoms on a PdMo bimetallene as a function of strain state. Reproduced with permission. Copyright 2019, Springer Nature.
over the Pd@Pt 1L, Pd@Pt 2-3L, PdH@Pt 1L, PdH@Pt 2-3L, PdH@Pt4-5L, and Pt octa catalysts. Similarly, the compressive
strain is also benefical for the HER of Pd. The Cu 45Pd45@Pd core–shell structured SRE has shown lower HER over-
potential in 0.5 m H 2SO 4 solution than the Pt/C catalyst,
although their Tafel slopes are quite similar. Theoretical cal-
culations proved the excellent HER performance of this
Cu45Pd45@Pd core–shell structured SRE is originated from
its extremely small ΔG H value (−0.01 eV).[183] On the other
hand, the tensile Pt-based SREs exhibited good HER per-
formance, mainly ascribed to the change of electronic struc-
tures of the Pt metal in the shell of these Pt-based SREs.
A core–shell structured catalyst, the electronic structure of
a metal in the shell is actually affected by both strain effect,
electronic effect, and ligand effect from the metal in the core.
For example, in a Pd 3Pb-core and a Pt-shell SRE (AL-Pt/
Pd3Pb), the lattice parameter of the Pd 3Pb-alloy core is larger
than that of standard Pt or a Pt layer (Figure 17e). [193] The ten-
sile strain is stretched near 3.6%. The HER overpotential of
this AL-Pt/Pd 3Pb SRE (13.8 mV) was much lower than that
of its counterpart Pt/C (30 mV) and Pd 3Pb (296 mV) catalysts
(Figure 12f). On the AL-Pt/Pd 3Pb SRE, an obvious electron
transform was found from Pd and Pb to Pt at the Pd 3Pb/Pt
interface. The energy of the d-band center of Pt atom at the
shell surface shifts to Fermi level via strain effect, leading to a
suitable ΔG H1 value and eventually high HER activity.

The Ru-based catalysts containing the strains have been
designed as the HER catalysts. In the case of a CoRu 0.5 alloy
nanoparticle,[194] the Co site is stretched since the atom radius of
a Co atom (126 pm) is shorter than that of a Ru atom (132 pm).
This CoRu0.5 SRE thus exhibited better HER performance than
a Pt/C catalyst and other CoRu X catalysts. Such improved HER
performance was assigned to the optimized strain states and
electronic structures of both Co and Ru sites in this CoRu 0.5
alloy. For a RuSi alloy,[205] the electronic structure of a Ru site
was optimized by adjusting the strain state via the addition of
Si dopant. The ΔG H value was then reduced on the Ru site.
This RuSi-alloy SRE exhibited better HER performance than a
Pt/C catalyst. N doped RuP nanoparticles were also synthesized
for HER. After N atoms are doped into a RuP nanoparticle
(N-RuP),[196] the length of a Ru-P bond in the N-RuP catalyst
(2.37 Å) is larger than that (2.32 Å) in a standard RuP cata-
lyst (Figure 17g). A tensile strain is thus formed in the N-RuP
catalyst (Figure 17h). In 0.5 m H 2SO 4 solution, the N-RuP SRE
exhibited a small HER overpotential (0 mV), much smaller
than that obtained on the RuP (5 mV) and Ru (22 mV) catalysts
(Figure 17i). These values confirmed a suitable ΔG H1 value on
the N-RuP SRE.

Figure 17. a) HER free energy barriers. b) The volcano plot of hydrogen adsorption energy (ΔG H*) on the metal surfaces versus HER activity (j0). Repro-
duced with permission.[8] Copyright 2017, American Association for the Advancement of Science. c) HAADF-STEM image of a Ru@Pt nanoparticle.
d) EXAFS spectra of a Ru@Pt catalyst, a RuPt alloy, and a Pt foil. Reproduced with permission.[191] Copyright 2018, American Chemical Society.
e) HAADF-STEM image and f) HER polarization curves of an AL-Pt/Pd 3Pb catalyst. Reproduced with permission.[193] Copyright 2019, American Chem-
ical Society. g) Illustration of the N atom doping to RuP. h) EXAFS spectra and i) HER polarization curves of the N-RuP/NPC catalyst and its contrast
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The transition metal dichalcogenides (such as, MoS$_2$) are potential substitute HER catalysts due to their good performance, it is clear that a tensile strain is necessary for the enhancing of the $\Delta G_{H}^{\text{H}}$ of MoS$_2$ to get better HER performance. Previous DFT studies proved the acceleration effect of tensile strain and S vacancy on MoS$_2$ toward HER.[94] The tensile strain facilitates the adsorption of hydrogen atoms on the MoS$_2$ catalyst. A higher concentration of the S vacancy results in stronger adsorption of hydrogen atoms on the catalyst surface. Moreover, the electrical conductivity was optimized by the tensile strain and the S vacancy. The experimental results are in good line with the predictions from theoretical calculations. Namely, the MoS$_2$ catalyst with both a tensile strain and a higher concentration of S vacancy exhibited lower HER overpotential than the MoS$_2$ catalysts that only owned the tensile strain or the S vacancy, as well as, the pure MoS$_2$ catalyst. The HER performance of defective Ni-MoS$_2$ was also investigated,[206] where the half Mo atom is replaced by Ni atom orderly. The optimized lattice spacing of Ni-MoS$_2$ (3.351 Å) is among the lattice spacing of NiS$_2$ (3.54 Å) and 2H-MoS$_2$ (3.192 Å). Compare to the MoS$_2$, the HER overpotential of Ni-MoS$_2$ is optimized. Nevertheless, the $\Delta G_{H}^{\text{H}}$ of Ni-MoS$_2$ still needed to be strengthened namely the tensile strain and S vacancy are needed. According to the calculated result, the best tensile strain is between 11% ($\Delta G_{H}^{\text{H}} = 0.018$ eV) and 12% ($\Delta G_{H}^{\text{H}} = -0.025$ eV). Besides, the bandgap energy is also decreased when the Ni-MoS$_2$ is stretched. Eventually, the semiconductor Ni-MoS$_2$ (no strain) transforms to metal Ni-MoS$_2$ (11%). As for a Ni-MoS$_2$ with no strain but 2.5% S vacancy, the $\Delta G_{H}^{\text{H}}$ value is close to 0 eV. Such a strain state and S vacancy concentrate on Ni-MoS$_2$ are easier to be achieved when compare with the pure MoS$_2$.[94] The Ni-MoS$_2$ has better HER performance adjustability than MoS$_2$. Hence, the MoS$_2$ based HER catalyst design can be introducing tensile strain, S vacancy, and transition metal doping. Based on this mechanism, a series of MoS$_2$ catalysts have been synthesized and applied as the HER catalysts to achieve commendable HER performance (Table 2).[195,207,208]

The utilization of SREs for the HER in alkaline solutions is still immaturity. Compared to those in acidic solutions, the HER processes in alkaline media are known to be more sluggish. This is because the HER processes in alkaline solutions begin from the formation of H* and OH* intermediates by the dissolution of adsorbed H$_2$O* intermediate. Due to a large reaction barrier, the formation of H* radical is much more difficult in alkaline solutions than in acidic solutions. A H$_2$ molecule is then formed via coupling H* with a H* or a H atom from an adsorbed H$_2$O* intermediate. For the HER catalyst design in alkaline solutions, decreasing the energy barriers of

### Table 2. Performance of different SREs toward the HER in acidic, neutral, and alkaline conditions.

| Catalyst | Electrolyte | Overpotential (mV @ 10 mA cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | Ref. |
|----------|-------------|-----------------------------------|-----------------------------|-----|
| 1 Ru@Pt  | 0.5 m H$_2$SO$_4$ | 1 mV @ 1 mA cm$^{-2}$ | 30 [191] |
| 2 WO$_x$-PtNi@Pt DNWs | 0.1 m KOH | 24 X [161] |
| 3 Pd@Pt$_{0.8}$ | 0.5 m H$_2$SO$_4$ | 13.8 18 [193] |
| 4 AL-Pt/Pd-Pb | 0.5 m H$_2$SO$_4$ | 0.1 m KOH 5 X [52] |
| 5 CuPD@Pd | 0.5 m KOH | 10 X [183] |
| 6 PD@Ir | 0.1 m KOH | 20 X [197] |
| 7 Au@AuIr$_3$ | 0.5 m H$_2$SO$_4$ | 29 15.6 [141] |
| 8 IrNi | 1 m KOH | 17 79 [117] |
| 9 PdCoO$_2$ | 1 m KOH | 12 X [200] |
| 10 L-Ag | 0.5 m H$_2$SO$_4$ | 32 31 [201] |
| 11 SLNP | 1 m KOH | 8 X [202] |
| 12 CoRu$_{0.5}$/CQDs | 1 m KOH | 18 38.5 [194] |
| 13 N-RuP | 0.5 m H$_2$SO$_4$ | 20.5 X [196] |
| 14 Ru/np-MoS$_2$ | 1 m KOH | 30 31 [126] |
| 15 L-MoS$_2$-15 | 0.5 m H$_2$SO$_4$ | 220 62 [195] |
| 16 CoS@MoS$_2$-1L | 0.5 m H$_2$SO$_4$ | 95 71 [203] |
| 17 S@Co-D T 1T MoS$_2$ | 0.5 m H$_2$SO$_4$ | 42 32 [204] |
| 18 Pt@Ru | 0.1 m KOH | 7 X [198] |
| 19 Ag-Co$_{0.8}$O$_{1.2}$ | 1 m KOH | 51 49 [199] |

*PBS: phosphate buffered saline.*
water dissolution and regulating the $\Delta G_H$ value are thus both important.\cite{209} In the literature, although the effectiveness of strain regulation toward these $\Delta G_H$ value has been proved, the effect of strain toward the energy barrier of water dissolution is still puzzling. According to the Brønsted-Evans-Polanyi relation, enhancing the binding energies of H* and OH* intermediates can decrease the energy barrier of water dissolution.\cite{210} For example, Rh has a suitable $\Delta G_H$ value and stronger binding energy of $\Delta G_{OH}$ than Pt and thus shows lower overpotential toward the HER than Pt in alkaline media. A 3D volcano plot of the HER activity was thus proposed to guide the SRE design in alkaline solutions (Figure 18a).\cite{210} The best binding energies of the OH* and H* intermediates are $-0.3$ and $0$ eV, respectively. An investigation of the HER of Pt (111)/Ru (111) was in good line with this theory, where Ru atoms were modified on the Pt surface.\cite{198} The Ru skin was tensile ($-1.10$ eV) and had a positive $d$-band center than the Pt core ($-2.24$ eV). The tensile strain both enhanced the binding energies of $\Delta G_{OH}$ and $\Delta G_H$. Therefore, the energy barrier of water dissolution was decreased, and the $\Delta G_H$ value shifted to $0$ eV. This SRE exhibited lower overpotential than the Pt/C electrocatalyst in alkaline solutions (Figure 18d).\cite{185} When the $\Delta G_H$ value of a HER electrocatalyst is smaller than $0$ eV, while the binding energy of $\Delta G_{OH}$ is larger than $-0.3$ eV (e.g., Pt), the SRE design is incompatible since the strain simultaneously increases or decreases the binding energies of $\Delta G_{OH}$ and $\Delta G_H$. In this regard, some contradictory results about the HER performance on SREs have been reported. For example, a Cu$_3$Pt@Pt electrocatalyst that owns the compressive strain reduced the HER activity because the compressive strain decreased the strength of the Pt–OH bond.\cite{185} On the contrary, the compressive Pt skin showed lower HER overpotential than the Pt/C catalyst in other cases, the same performance as that obtained in acidic solutions.\cite{191,161,192}

### 3.3. Oxygen Evolution Reaction

The OER is the anodic half-reaction in the course of water splitting.\cite{211} This reaction is kinetically sluggish, due to the involvement of multiple electrons and/or protons. In general, H$_2$O is first adsorbed on an active site, followed by the formation of three intermediates (namely OH*, O*, OOH*) in sequence, finally into O$_2$ molecule during the OER process. Such a process is called an adsorbate evolution mechanism (AEM). Based on the volcano curve of the AEM mechanism, IrO2 and RuO2 are
the most potential OER catalysts (Figure 19a). A tensile strain is thus beneficial for the OER performance of RuO$_2$ because the binding energy of $\Delta G_0$ sits in the right leg of the volcano plot. A Ru core RuO$_2$ shell (Ru@RuO$_2$-L) catalyst is synthesized by laser irradiation of commercial RuO$_2$ powders and a near 6% tensile strain is observed on RuO$_2$ shell.[212] The OER overpotential of Ru@RuO$_2$-L (191 mV) is smaller than the overpotential of RuO$_2$ (280 mV) with no strain, which proved the acceleration effect of tensile strain in RuO$_2$ toward OER.

Note that the $\Delta G_{OH}$ value of the Ir electrocatalysts ($\approx$ 0.45 eV, Figure 14b) is far from the best theoretical binding energy (1.6 eV), although they especially the Ir electrocatalysts with a core–shell structure still showed good OER performance in many cases. One fact behind their good OER performance is that these Ir electrocatalysts were oxidized during the OER. Therefore, strain engineering of metal Ir has been applied to synthesize novel Ir SRES.[19,209,213–215] For example, in a nanoparticle with a PdCu-alloy core and a Ir shell (PdCu@Ir) (Figure 19b),[209] a compressive strain was noticed in the Ir shell. This is due to a smaller lattice parameter of a PdCu-alloy core than that of a Ir shell. In acidic solutions, the OER overpotential on this PdCu@Ir SRE was much smaller than that of Ir/C, PdCuIr/C, and PdCu/C electrocatalysts (Figure 19c). In another case, a core–shell structured Pd@Ir SRE was designed and synthesized using a seed growth method.[213] The Ir shells with adjustable layer numbers have been grown on a Pd-nanocube core. Since the Pd cube core has a smaller lattice parameter than the Ir shell, the Ir shell was compressive. Moreover, the Ir (100) facet on the shell was exposed, induced by the Pd cube core. This Pd@Ir$_{1L}$ SRE exhibited lower OER overpotential than the Pd@Ir$_{4L}$, Pd@Ir$_{3L}$, Pd@Ir$_{2L}$, and Ir/C electrocatalysts, although the Pd@Ir$_{4L}$ and Pd@Ir$_{3L}$ electrocatalysts had higher Ir atomic efficiencies (Figure 19d). Consequently, controlling the strain state by regulating the shell layers is crucial for the enhancement of intrinsic OER activity in a core–shell catalyst. By controlling the shape of a Pd core, the Pd@Ir cube, Pd@Ir octahedron, Pd@Ir trioctahedral were also synthesized as OER electrocatalysts. The Pd@Ir trioctahedral showed lower overpotential than Pd@Ir cube, Pd@Ir octahedron, and Ir/C electrocatalysts (Figure 19e-f).[216] In conclusion, the compressive strain inside the Ir-SREs is beneficial to decrease their binding natures with $O^*$, $OH^*$, $OOH^*$ and thus to accelerate their OER performance, although they are oxidized during the OER.

To reduce the cost of the Ir and Ru-based catalysts, the non-noble OER SREs have been developed. For example, a NiFe hydroxide electrocatalyst with a tensile strain has been
synthesized by a ball-milling method.\textsuperscript{[217]} This NiFe hydroxide SRE exhibited enhanced OER performance than the fresh NiFe hydroxide. This is because the O intermediate can be strongly adsorbed on this NiFe hydroxide SRE. Such stronger adsorption of O* makes the energy barrier of the OER shift to a lower value. This accelerated effect from a tensile strain in the NiFe hydroxide electrocatalyst has also been seen in the NiFe-MOF electrocatalyst, synthesized by a solvent reduction method and a subsequent irradiation process by use of ultraviolet light. The tensile strains of as-synthesized electrocatalysts can be regulated from 0\% to 4.3\% (Figure 19g).\textsuperscript{[218]} The NiFe-MOF electrocatalyst with a tensile strain of 4.3\% exhibited better OER performance than other NiFe-MOF-X\% (X = 0, 1.7\%, 3.6\%) and benchmarked RuO\textsubscript{2} electrocatalysts, resulting from a lower free energy barrier of the OER on this SRE.

Note that a lattice oxygen mediated mechanism (LOM) is also available to describe the performance of different OER electrocatalysts. In this OER mechanism, the O\textsubscript{2} is formed by coupling the formatted O* and O atom in metal oxide rather than dehydrogenation of OOH*. When the Ni atom was introduced to the lattice of tensile RuO\textsubscript{2} shell of Ru@RuO\textsubscript{2}, its OER overpotential decreased obviously. The isotope labeling experiment proved the OER on Ni-Ru@RuO\textsubscript{2} is a LOM process. LOM leads to a lower energy barrier during OER for Ni-Ru@RuO\textsubscript{2}, which is the main reason for its good OER activity.

3.4. Alcohol Oxidation Reaction

A direction alcohol fuel cell (DAFC) converts the chemical energy of alcohols to electrical energy with low emission. Numerous advantages of using alcohols as fuels (e.g., high energy densities, high security, and high convenience) make a DAFC be a promising electrochemical energy conversion process.\textsuperscript{[221]}

![Figure 20.](image-url)

**Figure 20.** a) Possible reaction pathways of the MOR. Reproduced with permission.\textsuperscript{[146]} Copyright 2021, Wiley-VCH. HAADF-STEM images of b) c-PdH\textsubscript{0.43}@Pt and c) o-PdH\textsubscript{0.43}@Pt. d) MOR cycle voltammograms on the c-PdH@Pt, o-PdH@Pt, c-PdH\textsubscript{0.43}@Pt, o-PdH\textsubscript{0.43}@Pt, and Pt/C catalysts. Reproduced with permission.\textsuperscript{[221]} Copyright 2007, American Chemical Society. e) HRTEM image of a Pt\textsubscript{3}Ga@Pt catalyst. f) MOR cyclic voltammograms (CVs) on the Pt\textsubscript{3}Ga@Pt (blue), Pt nanocube (red), and commercial Pt/C catalysts (black). g) MOR free energies on the Pt (100) and stretched Pt (100) facets. Reproduced with permission.\textsuperscript{[223]} Copyright 2018, American Chemical Society. h) The HRTEM image of an Au@PtNi catalyst. i) MOR CVs of the Au@PdPt, PdPt alloy, Pt, and AuPt catalysts. Reproduced with permission.\textsuperscript{[146]} Copyright 2021, Wiley-VCH.
Although direct oxidation of alcohols (e.g., methanol, ethanol) at the anode of a DAFC can produce many electrons (e.g., direct oxidation of methanol into CO₂ involves six electrons), this kind of oxidation reaction is kinetically sluggish. The design and synthesis of different AOR electrocatalysts are thus of great importance and urgently desired to achieve high-performance DAFCs.

3.4.1. Methanol Oxidation Reaction

The MOR can happen in different pathways (Figure 20a): A CO pathway (red line) or a HCOOH pathway (black line). On the most common or the bench-marked MOR electrocatalyst—the Pt/C catalyst, the MOR tends to go through a CO pathway. This is due to a relatively lower reaction barrier of a CO pathway than that of a HCOOH pathway. Namely, the rate-determining step during the MOR on the Pt/C electrocatalyst is the conversion from CO⁺ to COOH⁺, where the adsorbed CO⁺ intermediate must first be combined with an adsorbed OH⁻ intermediate, followed by the formation of a COOH⁻ intermediate. The tensile strain in a Pt electrocatalyst is thus beneficial to improve the MOR performance, because of strong adsorption ability of a tensile Pt electrocatalyst toward an OH⁻ intermediate. For example, a Pt monolayer has been deposited on the surfaces of single Au (111), Pd (111), Rh (111), Ru (0001), and Ir (111) crystals.[220] The Pt₃Ga/Au(111) electrocatalyst exhibited higher MOR activity than other electrocatalysts and the Pt/C electrocatalyst. The compressive Pt monolayer even exhibited lower MOR activity than several Pt (111) electrocatalysts, including the Pd@Pt(111), Ir@Pt (111), Rh@Pt (111), and Ru@Pt (111) electrocatalysts. The DFT simulations provided a nearly linear relation between the MOR activity and the surface strain state of a Pt monolayer. Recently, the compressive Pt (100) skin on Pd@Pt nanocube (c-Pd@Pt) and compressive Pt (111) skin on Pd@Pt octahedron (o-Pd@Pt) were synthesized and exhibited poor MOR activity as expected.[221] To prepare tensile Pt skins, the H atom intercalation process was carried out to prepare the PdH₀.₄₃@Pt nanocube (c-PdH₀.₄₃@Pt) and compressive Pt (111) skin on Pd@Pt octahedron (o-Pd@Pt) were synthesized and exhibited much higher MOR activity as expected.[221] To prepare tensile Pt skins, the H atom intercalation process was carried out to prepare the PdH₀.₄₃@Pt nanocube (c-PdH₀.₄₃@Pt, Figure 20b) and PdH₀.₄₀@Pt octahedron (o-PdH₀.₄₀@Pt, Figure 20c) SREs. The c-PdH₀.₄₃@Pt and o-PdH₀.₄₀@Pt thus exhibited much higher MOR activity than c-Pd@Pt and o-Pd@Pt (Figure 20d) due to their stronger adsorption ability toward OH⁻ intermediate. Similarly, the tensile Pt shell in the Au@Pt and Ag@Pt electrocatalysts exhibited satisfied MOR performance.[46,222,223] When the metal in the shell is changed to a PtNi alloy, the tensile strain effect appears. An Au core thus further facilitates the MOR activity of the PtNi electrocatalysts. For instance, the catalyst with an Au-core and a PtNi-alloy shell (AuPtNi) has been prepared with a template method. This SRE exhibited 3.3-times higher MOR activity than the Pt/C electrocatalyst. This strategy was also found to be doable on the Pt-based SREs. The tensile Pt sites in the Ag@Pd[48] and Au@Pd[224] electrocatalysts exhibited enhanced MOR activity when compared with these electrocatalysts without strains.

In addition to pure metal cores (e.g., Au, Ag), a Pt₃Ga alloy has acted as the core. Due to a larger lattice parameter of a Pt₃Ga alloy than that of a Pt atom, a tensile Pt₃Ga@Pt catalyst has been prepared (Figure 20e).[225] Due to a tensile Pt shell (skin), this Pt₃Ga@Pt SRE exhibited higher MOR activity than Pt nanocubes and commercial Pt/C catalysts (Figure 20f). This is because of a lower MOR energy barrier of a tensile Pt (100) facet than that of a Pt (100) facet, or a stronger adsorption ability of a tensile Pt (100) facet toward OH⁻ intermediates than that of a Pt (100) facet (Figure 20g). Recently, a core–shell structured Au@PdPt electrocatalyst was synthesized via epitaxial growth of a PdPt-alloy shell onto an Au-nanorod core (Figure 20h).[146] The tensile strain was found to exist in this electrocatalyst. The synthesized PdPt alloy is stretched, stemming from the strong interaction between the PdPt shell and the Au core. This Au@PdPt SRE showed 9.4-times higher MOR activity than Pt/C and Pd/C catalysts as well as a PdPt/C alloy (Figure 20i).[146] Due to the stronger adsorption natures of the tensile PdPt (100) facet toward carbonaceous intermediates or a low MOR energy barrier, a HCOOH reaction pathway occurs on this Au@PdPt SRE, instead of a CO reaction pathway. Such a pathway was quite different from that on a Pt/C catalyst. It is worth mentioning that these SREs minimize CO position effect during the MOR in that on them the reaction of CO⁺→COOH⁺ is accelerated. Consequently, strain engineering of an electrocatalyst helps to regulate the reaction pathways of the MOR. The minimized CO position effect together with maximized alcohol oxidation activity during the MOR can be eventually realized on these SREs.

Tensile Pd and Pt sites in core–shell structured electrocatalysts always exhibited enhanced MOR activity. Interestingly, many Pd and Pt-based alloys (e.g., PtNi,[226] PtRh,[227] PtRu,[228] and PtCo[229]) also exhibited high MOR activity, although there are compressive strains in these catalysts. Such improved MOR performance is probably attributed to the fact that the MOR is a multiple-site reaction,[48,230] which is different from ORR, HER, and OER. Consequently, it is necessary to combine strain effect and synergetic effect of multiple sites during the performance analysis of used SREs. More precise ex situ and in situ spectroscopic studies need to be carried out to identify the MOR reaction pathways and further to clarify the relationship between the strain states in the SREs and reaction pathways of the MOR on these SREs.

3.4.2. Ethanol Oxidation Reaction

Different from the MOR, a complete EOR releases more energy since it can accompany 12 electrons. However, such a multi-electron transfer process is dynamically sluggish. Moreover, the oxidation selectivity of the EOR is generally poor, resulting in poor efficiency of the EOR. For example, ethanol tends to be oxidized into acetate, rather than CO₂. On the Pd/C, Pt/C, and Rh/C electrocatalysts, the percentages of the generation of CO₂ is only about 3%, 1–7%, 4%, respectively (Figure 21a).[231,232] Different electrocatalysts, especially SREs have been thus designed and synthesized in past years to enhance their oxidation activity and CO₂ selectivity during the EOR. For example, many tensile electrocatalysts (e.g., Pt-, Pd-, and Rh-based catalysts) exhibited enhanced cleavage ability of the C–C bond. For example, a core–shell PtBi@Pt cluster catalyst has been designed for the EOR (Figure 21b). Since the lattice parameter of its core is larger than that of the Pt shell, the Bi atom doped into the Pt core makes the Pt shell tensile.[233] As expected,
this SRE exhibited higher EOR activity and CO₂ selectivity than a Pt/C catalyst. The synthesis of an EOR SRE with an Ag core and a Pd shell has been realized by use of a two-step solvothermal reduction method. The size of this SRE and the layer thickness of the Pd shell were further controlled. The Ag@Pd₂ SRE exhibited good EOR activity as well as a high cleavage percentage of the C=C bond (up to 18%). After doping of this thin Pd layer with a P dopant, the Ag@Pd₂P₀.2 SRE displayed improved EOR mass activity (Figure 21c) and an even higher cleavage percentage of the C=C bond than its counterparts (Figure 21d,e). The DFT calculations demonstrated that the electronic structure of the Ag@Pd₂P₀.2 SRE is modified by the Ag core and the doped P atoms. The tensile Pd layer in this core–shell structured catalyst has a lower energy barrier to...
cleavage the C–C bond of CH₃CO, a key intermediate during the EOR.

Similar to the SRE with an Ag core and a Pd shell, the electrocatalyst with an Au core and a Pt shell was found to be beneficial for the cleavage of C–C bond during the EOR. The Au@PtIr core–shell structured catalyst, prepared via the growth of a PtIr-alloy shell on the prepared Au/C catalyst, exhibited 8.4-times higher catalytic activity than the Au@Pt and the benchmarked Pt/C catalysts (Figure 21f). The achieved cleavage percentage of the C–C bond was up to 57%. Such high EOR performance on this SRE was attributed to a tensile strain of the PtIr shell-layer that was induced by the Au core. In the Rh catalyst with a nano-branch structure, a tensile lattice strain was found (Figure 21g). This SRE exhibited both higher EOR activity (Figure 21h) and faster CO₂ production rate than contrasticosahedral Rh and tetrahedral Rh nanocatalysts as well as commercial Rh black catalyst (Figure 21i). In short, the Pd, Pt, and Rh catalysts with tensile strains accelerate the cleavage of the C–C bond more efficiently than those without strains. Improved EOR activity and enhanced CO₂ selectivity during the EOR are thus possible on different kinds of SREs (e.g., core–shell structured electrocatalysts, alloys). However, the efficiency of the cleavage of the C–C bond on these SREs still needs to be further improved. The unclear relation between the cleavage efficiencies of C–C bond and tensile strains of SREs should be revealed to fully clarify the EOR pathways. In short, deeper studies on the design, synthesis, and properties of SREs as well as their EOR performance need to be conducted.

3.5. Electrochemical CO₂ Reduction Reaction

Electrochemical CO₂ reduction reaction (ECO₂RR) is a novel approach to electrosynthesize value-added chemicals (e.g., CO) and liquid fuels (e.g., CH₃OH, C₂H₅OH) from earth-rich and greenhouse gas—carbon dioxide. It thus belongs to an important and sustainable conversion technology in the carbon cycling process. To stimulate inert CO₂ and further improve the selectivity of reduction products during the ECO₂RR, an electrocatalyst is always required. Knowing the mechanism of ECO₂RR is of great importance for ECO₂RR catalyst design. As is mentioned above, the scaling relation exists in ECO₂RR to CH₄. Except for CH₄, the CO₂ can also be reduced to other C₁ products (CO, HCOOH, and CH₃OH). The two C₁ products CO and HCOOH are competitive. The intermediate of HCOO* is crucial for producing HCOOH, while the COOH* is the key intermediate for producing CO. The binding energies of these two intermediates have no relation because the different bond

Figure 22. a) The activity volcano plot of ECO₂RR to HCOOH, the binding energy of HCOO* is a descriptor. Reproduced with permission. Copyright 2017, American Chemical Society. b) HRTEM image of a Bi@Sn catalyst. c) Product selectivity of the ECO₂RR on the Bi@Sn and Sn catalysts. Reproduced with permission. Copyright 2020, Wiley-VCH. d) The strain mapping of Pd octahedral and icosahedral nanoparticles. e) The d-band electron state of a Pd (111) facet with different strain states. f) The free energy barrier of the ECO₂RR on a Pd (111) facet with different strain states. Reproduced with permission. Copyright 2017, Wiley-VCH. g) Synthesis steps, h) TEM image, i) EXAFS spectra of a Pd₆@Au catalyst. Reproduced with permission. Copyright 2019, American Chemical Society.
types of HCOO\(^*\) (O\(=\)M) and COOH\(^*\) (C\(=\)M) are different.\(^{2,26}\) Therefore, the designing of ECO\(_2\)RR catalysts with high selectivity of HCOOH needs to tune the binding energy of HCOO\(^*\) and COOH\(^*\). A volcano plot of the activity of ECO\(_2\)RR to HCOOH based on the binding energy of HCOO\(^*\) is proposed (Figure 22a). Besides, the restrain of HER during ECO\(_2\)RR in a high overpotential range is also necessary. In this context, the compressive strain is possible to enhance the ECO\(_2\)RR performance of Bi-based catalysts which was reported as a suitable catalyst for selectivity reduce CO\(_2\) to HCOOH.\(^{2,27,238}\) On a catalyst with a Bi-core and an Sn-shell (Bi@Sn),\(^{2,39}\) a compressive strain was noticed in the Sn shell. The Sn shell exhibits a smaller plane spacing (0.283 nm) of an Sn (020) facet than that (0.291 nm) of a standard Sn (020) facet (Figure 22b). Such a change is induced by the Bi core. This Bi@Sn catalyst exhibited improved HCOOH selectivity and higher current density within the potential range from −0.8 to −1.2 V (vs RHE) than the Sn nanoparticles (Figure 22c), an indication of a lower ECO\(_2\)RR free energy barrier on the compressive Sn shell. The binding energies of both HCOO\(^*\), COOH\(^*\), and H\(^*\) decreased due to compressive, while the free energy barrier difference value between HCOOH and CO and H\(_2\) increased, which is the reason for compressive strain enhancing selectivity of HCOOH.

Selectivity producing CO during ECO\(_2\)RR is more complex than HCOOH due to the limiting of CO\(_2\)-desorption. Based on the scaling relations, the Au is the best candidate for selectively reduce CO\(_2\) to CO, and the tensile strain needed to decrease the overpotential of CO\(_2\) to CO.\(^{2,26}\) However, the lattice parameter of Au is larger than other fcc metals. Namely, the tensile strain in Au is difficult to achieve. In an AuCu\(_3@Au\) nanoparticle, due to the lattice mismatching between fct AuCu\(_3\) core and Au shell, the 3D lattice constants of the Au shell are 3.92, 3.92, and 4.36 Å, respectively, which is compressive in X and Y axes while tensile in Z axis compares with Au (4.079 Å in three dimensions). Affected by the anisotropic strains, the Au shell exhibited higher CO selectivity in ECO\(_2\)RR than fcc Au.\(^{2,40}\) The d-band center of Au shell (−3.584 eV) is positive than fcc Au (−4.082 eV), the free energy barrier of CO\(_2\) to CO is thus lower than fcc Au. In many cases, Pd-based catalysts have shown high CO selectivity during the ECO\(_2\)RR.\(^{2,43}\) Based on the scaling relation, tensile strain is beneficial for the energy barrier of CO\(_2\) to CO while a compressive strain is beneficial for the energy barrier of CO desorption. Therefore, the design of Pd-based catalyst is contradictory from the aspect of strain because the energy barriers of the electrochemical process and thermodynamics process are incommensurable. In many experiment cases, the tensile strain is proved beneficial for CO\(_2\) reduction to CO. For example, a Pd icosahedral nanoparticle with a tensile strain of about 1.8% exhibited higher CO selectivity within a wide potential range than a compressive Pd octahedral nanoparticle with a compressive strain of about −0.5%. There are no other effects (such as, ligand effect, alloy effect) because the strains on these Pd nanoparticles results from their different shape (Figure 22d).\(^{2,42}\) Moreover, the difference of these strains has led to varied energies of a d-band center in these nanoparticles. A Pd icosahedral nanoparticle shows a higher energy of a d-band center (Figure 22e). Consequently, the adsorption of CO\(^*\) and COOH\(^*\) on a Pd icosahedral nanoparticle is stronger than on a Pd octahedral nanoparticle. The free energy barrier of the formation of COOH\(^*\) is lower while the energy barrier of desorption of CO\(^*\) is higher on a Pd icosahedral than on a standard Pd or Pd octahedral nanoparticle (Figure 22f). Meanwhile, the tensile strain enhanced the \(A_{\text{H}}\) value on a Pd site and thus the HER was seriously hindered. In other words, after over consideration the three effects (CO\(_2\)→COOH\(^*\), CO\(^*\)→CO\(_{\text{ads}}\), and HER), the tensile strain on Pd is proposed to be beneficial to produce CO during the ECO\(_2\)RR. Based on these assumptions, a catalyst with an Au-core and a Pd-shell (Pd, @Au) was designed and synthesized to restrain the HER and simultaneously to enhance the CO selectivity during the ECO\(_2\)RR.\(^{2,44}\) The composition in the shell was further changed from an atomically dispersed PdAu alloy to a pure Pd shell (Figure 22g.h). The length of the Pd−Pd bond in the Pd, @Au catalyst was found longer than that in a standard Pd catalyst. This length is decreased when the Pd amount in the shell is increased (Figure 22i). All these Pd, @Au core−shell structured SREs exhibited higher current densities during the ECO\(_2\)RR than the Au- and Pd-catalysts. The accelerated ECO\(_2\)RR performance was attributed to the stronger adsorption of CO on the tensile Pd sites in these core−shell structured SREs. In a catalyst with a Pd-core and an Au-shell (M-AuPd(20)),\(^{2,46}\) the Pd-core exhibits strong tensile strain, resulted from the used MOF support. This tensile strain has remained even when the Pd-core is coated with an Au layer. This M-AuPd(20) SRE exhibited higher product selectivity toward HCOOH during the ECO\(_2\)RR than the M-Pd and Pd/C catalysts.

From the scaling relations, Cu is the best catalyst for electro-reducing CO\(_2\) to CH\(_4\). However, the limiting potential is lower than (−0.7 to −0.8 V), which leads to a high energy course during ECO\(_2\)RR. The breaking of such a scaling relation is important. The effects of the surface strain of Cu nanoparticles toward ECO\(_2\)RR were investigated by DFT.\(^{2,45}\) When using a metal core to change the surface strain of the Cu shell, the binding energies of CO\(^*\) and CHO\(^*\) are fitted by two liners with different strain states. The absolute value of the slope of CO\(^*\) to strain (−0.033) is much lower than CHO\(^*\) to strain (−0.139). The energy barrier of CO\(^*\) to CHO\(^*\) on an Au@Cu nanoparticle (0.81 eV) is smaller than on Cu (1.15 eV). Therefore, the tensile strain can break the scaling relation of ECO\(_2\)RR and is beneficial for the Cu-based catalyst performance of CO\(_2\) reduction to CH\(_4\). The experiment also confirms this prediction.\(^{2,46}\) As for a star-like decahedron Cu nanoparticles (SD-Cu), twin boundaries and multiple stacking faults were observed, which lead to a surface tensile strain of 1.128%. Benefits for the surface strain, the overpotential for formatting CH\(_4\) on SD-Cu is lower than commercial Cu nanoparticles for near 0.149 V. The ECO\(_2\)RR is complicated for Cu-based catalysts because there are also other kinds of C2 products. For example, the SD-Cu shows an FE of 52% for C\(_2\)H\(_4\) at −0.993V.\(^{2,46}\) The lattice strain also shows a strong ability to regulate the selectivity of C2 products. For example, the La\(_{2}\)CuO\(_4\) catalyst with a nanobamboo structure had a rich grain boundary.\(^{2,47}\) This fully tensile La\(_{2}\)CuO\(_4\) electrocatalyst exhibited higher product selectivity into C\(_2\)H\(_4\) during the ECO\(_2\)RR than the La\(_{2}\)CuO\(_4\) electrocatalyst with a bulk structure.

Although strain engineering has been proved to be an effective approach to design efficient and selective ECO\(_2\)RR electrocatalysts, the overpotential and selectivity of ECO\(_2\)RR are...
still insufficient. Since the ECO₂RR mechanisms are much more complicated than those of the OER, ORR, and HER, where more intermediates and multiple reaction pathways are involved during the ECO₂RR, further studies on different SREs are for sure required in the aspects of their synthesis, properties, and performance investigations toward the ECO₂RR.

3.6. Nitrogen Reduction Reaction

Nitrogen reduction or nitrogen fixation into ammonium is a burgeoning research topic. Electrochemical NRR is expected to dramatically reduce energy consumption. It is fully different from the synthesis of NH₃ by means of the Haber-Bosch method where a huge amount of energy is needed. However, the cleavage of a stable N≡N bond at room temperature is extremely difficult where complicated reduction processes are involved with very high energy barriers. In this regard, a suitable electrocatalyst is a prerequisite for high-performance NRR. Moreover, a large overpotential commonly exists during the NRR, resulting in serious occurrence of the HER side-reaction. To design high-performance NRR catalysts, both enhanced NRR activity and restrained HER activities must be considered.

According to the calculated NRR volcano curve (Figure 23a),[248] Rh, Ru, and Ir metals are proper catalysts for the NRR. However, they also feature high HER performance. To restrain the HER process, the compressive strain was then introduced to these NRR electrocatalysts. For example, a compressive MoS₂ electrocatalyst was synthesized through its doping with F dopant (F-MoS₂).[249] The spacing of the MoS₂ (002) facet on this F-MoS₂ electrocatalyst is slightly compressed in comparison to a standard MoS₂ catalyst. This is because of a smaller size and a higher electronegativity of a F atom than those of a S atom. As predicted, the HER activity of the F-MoS₂ SRE was worse than a MoS₂ catalyst (Figure 23b). However, it exhibited a higher current during the NRR than a MoS₂ catalyst (Figure 23c). Therefore, the compressive strain is beneficial to restrain the HER and meanwhile to accelerate the NRR. Such a statement is further supported by the calculated free energies of the NRR on the F-MoS₂ and MoS₂ electrocatalysts, namely the fact that the F-MoS₂ SRE has a lower energy barrier than a MoS₂ electrocatalyst for the NRR.[249] The MoS₂ catalyst deposited on CuS quantum dots has been utilized for the NRR (Figure 23d).[250] Among these core–shell structured electrocatalysts (e.g., from Cuₓ₋₁S(MoS₂)₁₀% to Cuₓ₋₁S(MoS₂)₁₀% and Cuₓ₋₁S(MoS₂)₂-5%), based on the atomic ratio of Cu to Mo, the Cuₓ₋₁S(MoS₂)₁₀% exhibited the fastest yield rate of NH₃ and the highest FE within a wide potential range. Its NRR performance was also superior over Cuₓ₋₁S quantum dots and other Cuₓ₋₁S(MoS₂)₁₀% (Y = 1, 5, 10) electrocatalysts. The DFT calculations confirmed a lower NRR free energy of the NRR on the Cuₓ₋₁S(MoS₂) SRE than that on the MoS₂ and Cuₓ₋₁S catalysts.

Such a strategy has been extended to other metal electrocatalysts (Figure 23e). For example, a nanoparticle with a CuAu-alloy core and a Cu-shell (CuAu@Cu) has been synthesized,[251] where the lattice parameter of the CuAl alloy core is larger than the Cu shell, leading to a tensile Cu shell (Figure 23f). The layer number of the Cu shell was further adjusted by controlling the amount of the used Cu precursor. On the SRE with a layer number of 2 in the Cu shell (CuAu@2LCS), the product yield rate of NH₃ was 34 g h⁻¹ mg cat⁻¹ and the FE reached 23% at −0.2 V (vs RHE). Such performance is much better than the electrocatalysts of Au, Cu, CuAu@0LCS (namely, without a Cu shell), and CuAu@4LCS (with a layer number of 4 in the Cu shell). For those Cu-based catalysts, the rate-determining step of the NRR was determined to be the reaction of N₂* to HNN*. The CuAu@2LCS SRE has stronger adsorption ability toward N₂ and a lower free energy barrier in the NRR rate-determining step than the CuAu@0LCS and CuAu@4LCS catalysts (Figure 23g). The synergy of strain effect and ligand effect in this CuAu@2LCS SRE contributes to such high NRR performance. A nano-catalyst with a Rh-core (6 nm in size) and a Sn-shell (Rh-Se NC) was synthesized by use of a two-step reduction method.[252] The Sn shell with a thickness of about 1.3 nm exhibits amorphous characteristics. It thus has a strain effect, which is induced by the Rh core. Within a potential range from −0.05 to −0.25 V (vs RHE), this Rh-Se NC SRE exhibited a much faster yield rate of NH₃ and a higher FE than the Rh and Se catalysts (Figure 23h). The HER process is restrained on the Rh-Se NC catalyst, more pronounced than that on the Rh and Se catalysts. Such improved NRR performance is due to a higher energy of d-band center of the Rh-Se NC. The NRR activity of TiO₂ has been enhanced by strain engineering of a TiO₂ catalyst.[253] For example, the tensile strain was introduced via electrochemical intercalation of Li(II) ions into TiO₂ nanotubes (s-TiO₂ NTs). The s-TiO₂ NTs exhibits a larger (101) lattice spacing (0.359 nm) and a more negative XRD pattern location (25.2°) than those of the TiO₂ nanotubes (0.350 nm and 25.5°, respectively) (Figure 23i). Affected by this tensile strain, the length of the N≡N triple-bond of adsorbed N₂ on the s-TiO₂ NTs (1.17 Å) is larger than that on the TiO₂ nanotubes (1.13 Å). In other words, the N₂ activation is accelerated on the s-TiO₂ NTs. A yield rate of NH₃ (5 g h⁻¹ cm⁻²) and a FE (26%) were thus obtained on the s-TiO₂ NTs (Figure 23j). They are only 1.8 g h⁻¹ cm⁻² and 18% on the TiO₂ nanotubes, respectively. The DFT calculations helped to conclude that the tensile strain in this SRE not only accelerates the activation of N₂ but also decreases the free energy barrier of the NRR (Figure 23k).[253]

Although several SREs have been utilized for the NRR, most of the reported NRR systems have the shortcomings of low activity and poor selectivity. For the NRR, there is still no benchmark SREs available. The sources of generating NH₃ products (e.g., the electrolyte, environment, catalyst) are hard to be separated and distinguished with an easy approach. In this regard, the design of high-performance SREs is the highest priority for the NRR activities.

4. Summary and Perspectives

Our society urgently needs better and more efficient electrochemical energy conversion technologies and systems to solve serious environmental and energy problems. For these technologies and systems, more advanced electrocatalysts must be designed, constructed, and explored. The SREs developed in the past years belong to them. These SREs do exhibit excellent catalytic performance toward various electrochemical reactions, including ORR, HER, OER, AOR, ECO₂RR, and NRR.
Moreover, some SREs are possible to be produced on large scales and with reasonable prices. These SREs are thus promising to be utilized for commercial or industrial development of electrochemical energy conversion technologies and systems. Consequently, the principles, synthesis methods, and applications of the SREs are overviewed in this article.

However, they are still many challenges existing for the SREs in the aspect of their synthesis, mechanism clarification, and application exploration (Figure 24). For example, controllable and economic synthesis methods for the mass-production of high-performance SREs are still challenging. On one hand, during the design and synthesis process, the morphology (e.g., size, length), shape (e.g., sheet, wire, particle), and component (e.g., dual, triple, and multiple) of a SRE seem possible to be accurately controlled, based on the SRE theories. On the other hand, the precise control of strain state of a SRE is actually hard. For example, the strain state of a core–shell structured SRE has been successfully controlled according to the regulation of the shell thickness or the lattice parameter of the core. This kind of SREs thus feature high catalytic performance and have been widely applied in different electrochemical reactions. However, the flaws in the commercial or industrial applications...
of these SREs are quite obvious. These SREs are still too expensive, especially for the ORR and the HER where noble metals are generally added. To replace or reduce the use of expensive noble metals for the synthesis of high-performance SREs, an efficient approach is to utilize core–shell structured materials. In such an approach, a thin Pt skin will be coated on a core from Au, Ag, Pd, or a noble metal alloy (e.g., PtM and PdM). In this way, the exposure efficiency or catalytic activity of Pt atoms can be also enhanced. Differently, the price of the SREs can be reduced by replacing the expensive (noble) metal core(s) with the non-noble metals (e.g., Cu, Ni, Co). Meanwhile, the poor stability of these cheap core–shell structured SREs has to be improved. Transition metal phosphates (TMPs) and transition metal carbides (TMCs) are proposed as the potential core candidates that they have better stability than pure metals in acidic and alkaline solutions. Moreover, TMPs and TMCs exhibit commendable catalytic performance toward different catalytic reactions (e.g., HER and OER). Note that the shortcoming of TMPs and TMCs—their more complicated structures than pure metals needs to be taken into consideration during the design and synthesis of the SREs using a TMP or a TMC as the core. It has to highlight that electrocatalysts with strains or defects are often at their nonequilibrium states and thus their nanostructures probably evolve during different reaction processes. Although some SREs were reported to display long-time stability, the stability of the electrocatalysts with abundant strains or defects needs to be carefully studied, especially when high current densities and/or high potentials are applied. Advanced in situ techniques (e.g., time-sequential TEM) are expected to be powerful tools to reveal the complex surface sites/states and the structural changes of these SREs during these different processes (e.g., HER, OER, ORR, ECO2RR, AOR, NRR).

The mechanisms of different SREs have not been understood. For example, there are local lattice strains near the defects in a defect-rich catalyst. The strain states in the nanoparticles with small sizes and in different shapes have not been revealed yet. The relationship between the structure, strain, and catalytic performance of different SREs is unclear. To reveal these mechanisms, different and advanced strain characterization techniques (e.g., in situ and ex situ tools) have been utilized. Current technologies are mainly based on HRTEM and XRD, which can only detect the strain state of a local area and an overall average state, respectively. More precise techniques are required to determine the strain state of a SRE as required. By means of different advanced in situ and ex situ tools, as well as, their integration, the relationship between catalytic performance of a SRE and its electronic structures (e.g., the d-band electronic structure) can be more deeply and better revealed.[44,54,146,165]

The strain engineering of an electrocatalyst has been proved to be successful to regulate different electrochemical reactions. These regulations are first based on the relation between strain, d-band center, and adsorption energies of intermediates. Since the existing volcano plots clearly describe the activity and binding energy of key intermediates during numerous electrochemical reactions, the activity of the SREs is possibly regulated using the strategy of lattice strain design, where some general rulers need to be taken into consideration. For example, compressive strain is beneficial for the Pt and Pd-based electrocatalysts toward the ORR and HER. Tensile strain is beneficial for the Pt and Pd-based electrocatalysts toward the AOR. Tensile strain is beneficial for the Pt-and Au-based electrocatalysts toward ECO2RR to CO. Moreover, the scaling relations can guide the SRE design on the one hand but result in inevitable overpotential of electrochemical reactions. On the other hand, the lattice strains, especially anisotropic strains in the core(fct)@shell(fcc) electrocatalysts have been proved to effectively break the scaling relations in these electrochemical reactions. For example, a series of Pt electrocatalysts with a core–shell structure exhibited lower overpotential toward the OER than the minimum overpotential (0.37 V) estimated from their scaling relations. However, a universal rule of scaling relations to break strain is still missing, especially for complicated reactions. Further efforts and attention should be made in this area, once precise SRE synthesis and theories become available. Besides, although the geometry of a pure catalyst is known to affect its catalytic performance individually, most of the current strain studies have ignored such an effect. For example, the tensile Pt, Pd, and Rh electrocatalysts have exhibited enhanced cleavage ability of C–C bond than individual Pt, Pd, and Rh electrocatalysts where no strain exists. Such enhancement was only attributed to the change of electronic structure, caused by the tensile strain. The change of geometry structure of this SRE has not been considered. However, a change of the geometric structure of a SRE accelerates the cleavage of the C–C bond during the EOR, which may also affect other electrochemical reactions (e.g., proton coupling during the HER and the coupling of C–C bond during the ECO2RR). Therefore, the geometric effect in the SREs must be clarified, which will be much beneficial for the SRE design. More importantly, most of the electrocatalytic reactions are conducted in aqueous media, namely H2O molecules are participated in these reactions (e.g., H2O* → OH*, OH* + CO2 → COOH*). It is known that the lattice strain of SREs affects the solvent molecules, eventually leading to altered performance of
investigated electrocatalytic reactions. However, the studies of the activation effect or the role of H2O molecules on the SRE performance have not been frequently performed. In these regards, machine learning needs to be performed to reveal different aspects (e.g., properties, performance, mechanism) of novel SREs toward different electrocatalytic reactions, such as detailed electronic structures of different SREs, their volcano curves (free energy barriers or adsorption energies) toward different catalytic reactions. In the aspects of examining lattice strains, electronic structures, adsorption energies, free energy barriers of different SREs, machine learning will be much more efficient than other approaches since it can reduce dramatically working time and meanwhile offer different kinds of possibilities. By use of machine learning, the general tendencies and potential rules existed in the SREs are easier and more effectively to be summarized. Together with the experimental results, highly efficient, cheap, and stable SREs are expected to be discovered and synthesized. With aid of advanced electron microscopy, spectroscopy, electrochemical techniques, strain-catalysis mechanisms can be clearly clarified and demonstrated.

After discovering inherent rules and designing more efficient SREs, more efforts need to contribute to the application exploration of novel SREs in different fields, including for electrochemical water splitting and fuel cells. Of special interest, the SREs are expected to exhibit superior performance for burgeoning electrochemical water splitting and fuel cells. Of special interest, the SREs are expected to exhibit superior performance for burgeoning electrochemical water splitting and fuel cells. Of special interest, the SREs are expected to exhibit superior performance for burgeoning electrochemical water splitting and fuel cells. Of special interest, the SREs are expected to exhibit superior performance for

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Conflict of Interest

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