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## Recent advances in the heteroatom doping of perovskite oxides for efficient electrocatalytic reactions

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Perovskite-type transition metal oxides have emerged as promising electrocatalysts for various electrocatalytic reactions owing to their low cost, compositional tunability and high stability. However, insufficient electrocatalytic activities of pristine perovskite oxides hinder their pathway towards real-world applications. The incorporation of heteroatoms into perovskite oxide structures has been regarded as an efficient way to improve the electrocatalytic performance. This minireview summarizes the recent advances in the heteroatom doping of perovskite oxides as efficient electrocatalysts for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). These heteroatom doping strategies are classified based on various types of doping sites. The mechanisms of improved electrocatalytic activities are discussed in detail within different doping sites and various kinds of dopants. Finally, the remaining challenges and perspectives are outlined for future developments of perovskite oxide-based catalysts.

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### 1. Introduction

With the accelerated depletion of fossil fuels and environmental issues, advanced energy conversion technologies have attracted considerable attention in academia and industry.<sup>1–9</sup> Among them, energy conversion based on electrocatalytic reactions is a promising strategy, which can convert energies efficiently and flexibly through chemical bond transitions.<sup>10–13</sup> Although noble metal (*e.g.*, Pt, Ir, Ru, Pd, and Rh) based cata-



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lysts have been widely used for electrochemical and renewable energy technologies,<sup>14–17</sup> their prohibitive cost and extreme scarcity hindered their large-scale applications in the energy conversion industry. Therefore, it is imperative to seek low-cost and Earth-abundant alternative catalysts with comparable electrocatalytic activities for commercial demands.<sup>4,18–24</sup>

Perovskite-type transition metal oxides with a general formula of  $ABO_3$  show high compositional tunability, where the A-site is generally occupied by a rare-earth/alkaline metal with 12-fold coordination and the B-site is occupied by a transition metal with 6-fold coordination with O atoms.<sup>25</sup> Due to their low cost, environmental friendliness, high catalytic stability and large potential window, perovskite oxides have been intensively studied as promising catalysts for multiple electrocatalytic reactions, such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), carbon dioxide reduction reaction ( $CO_2RR$ ), and nitrogen reduction reaction (NRR).<sup>26–30</sup> However, in most instances, the catalytic activities of perovskite oxides are incomparable to those of conventional noble metal catalysts. This is because disunited 3d orbitals of surface transition metal cations usually result in either too weak or too strong surface adsorption/desorption strength of reactants.<sup>31</sup> Meanwhile, the relatively low electrical conductivities of many perovskite oxides lead to a sluggish charge-transfer process and slow the electrocatalytic kinetics.<sup>32</sup> To curb these adverse factors, many strategies have been attempted to improve the electrocatalytic performance of perovskite oxide catalysts, including heteroatom doping,<sup>33,34</sup> interfacial engineering,<sup>35</sup> strain modulation,<sup>36,37</sup> and introduction of defects.<sup>38,39</sup>

Among these strategies, heteroatom doping is one of the most facile and effective methods to optimize the catalytic properties of perovskite oxides. By affecting the interaction between oxygen and B-site atoms, the doped heteroatoms can improve the coupling efficiency of active centers and intermediate reactants, leading to facilitated electrocatalytic reac-

tions.<sup>40</sup> In terms of the elemental composition of perovskite oxides, in principle, more than 30 and 50 kinds of elements in the periodic table have been found at the A- and B-sites in  $ABO_3$  perovskite oxides, respectively.<sup>25</sup> The great flexibility in composition determines the diversity of doped heteroatoms, which could be doped into different sites of the  $ABO_3$  perovskite oxides, namely, the A-site, B-site, O-site, and dual-sites. This results in various optimizing concepts, such as A-site doping can impact indirectly *via* activating the transition metal catalytic sites,<sup>41,42</sup> B-site doping can optimize the B-site catalytic activities *via* electron exchange between the heteroatoms and the intrinsic B-site cations of perovskite oxides,<sup>43,44</sup> O-site doping can create abundant oxygen vacancies to improve the electrical conductivity,<sup>45,46</sup> and dual-site doping can promote the multi-active sites synergistically.<sup>47</sup> Recently, various types of dopants have been studied, including heteroatoms doped into the A site (*e.g.*, Na, K, Sr, Ca, Yb, Ce and La),<sup>41,42,48–52</sup> B site (*e.g.*, Ru, Ir, Fe, Co, Ni, Mn, W, P, S and Si),<sup>34,53–59</sup> O site (*e.g.*, F, S, N and Cl),<sup>46,60–62</sup> and dual sites (*e.g.*, Sr&Fe and Fe&Sn).<sup>47,63,64</sup> Although some work on heteroatom-doped strategies for electrocatalysis has been outlined briefly as a branch of optimizing approaches,<sup>45,65,66</sup> a few reports are systematically and comprehensively concerned with reviewing perovskite oxide electrocatalysts from the aspect of different doping sites. An up-to-date summarization of the latest discoveries and achievements is indispensable.

Herein, this minireview focuses on the recent advances in heteroatom doping strategies for the design of perovskite oxides towards efficient electrocatalytic reactions. These heteroatom doping strategies are classified based on the various types of doping sites, namely, A site, B site, O site and dual sites in perovskite oxides. The mechanisms of improved electrocatalytic activity are discussed in detail within different doping sites for three important electrocatalytic reactions, namely, the HER, OER, and ORR (Fig. 1). The current challenges and future perspectives are also outlined. This minire-



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Fig. 1 Schematic illustration of the A-site, B-site, O-site and dual-site heteroatom doping of  $ABO_3$ -type perovskite oxides for efficient electrocatalytic reactions including the HER, OER and ORR.

view aims to provide general guidelines and timely viewpoints for the design of highly efficient perovskite oxide catalysts based on heteroatom doping approaches.

## 2. A-site cation doping

Generally, the A-site cations in the pristine perovskite oxide structures are considered not to participate in the electrocatalytic process.<sup>45</sup> However, it will indirectly affect the electrocatalytic performance *via* activating the transition metal catalytic sites. In previous works, many heteroatoms have been doped into A sites to tailor the electronic structures, and

thereby to enhance the electrocatalytic activities of perovskite oxides. Accordingly, the effects of A-site doping in perovskite oxides on the electrocatalytic activities will be summarized based on the categories of doped heteroatoms, including alkali metals (*e.g.*,  $Na^+$  and  $K^+$ ),<sup>48,49</sup> alkaline-earth metals (*e.g.*,  $Sr^{2+}$  and  $Ca^{2+}$ ),<sup>50,67</sup> and rare-earth metals (*e.g.*,  $Yb^{3+}$ ,  $Ce^{3+}$  and  $La^{3+}$ ).<sup>41,42,52</sup>

### 2.1 A-site doping with alkali metals

Acting as p-type dopants, alkali metals usually have a lower valence of +1 and smaller size than the A-site cations of perovskite oxides. Among them,  $Na^+$  and  $K^+$  are widely adopted to modify the A-site and tailor the properties of perovskite oxides both physically and chemically. For example, the significant volumetric mismatch between  $Na^+/K^+$  dopants and A-site metal cations of perovskite oxides will result in lattice rearrangements.<sup>48</sup> Besides, the alkali metal dopants with a lower valence than the A-site metal cations in perovskite oxides will increase oxygen vacancies or change the oxidation state of B-site active centers owing to charge compensation effects.<sup>67</sup> All of these structural changes can effectively manipulate the electrocatalytic activity and durability.

Pavone *et al.* proposed K-doped  $Sr_2Fe_{1.5}Mo_{0.5}O_6$  (KSFMO) (Fig. 2a) as an excellent bifunctional catalyst for both the OER and ORR *via* first principles calculations.<sup>48</sup> They analyzed the structural and electronic features of both  $Sr_{1.5}Fe_{1.5}Mo_{1.5}O_6$  (SFMO) and KSFMO. In the SFMO/KSFMO topmost surface layer, the oxygen vacancies ( $V_O$ ) have two different environments due to different adjacent atoms, *i.e.*,  $Fe-V_O-Fe$  (Fig. 2b)



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**Fig. 2** (a) Structure of the 9-layer slab of KSFMO. Lateral and top views of the outermost layers after the formation of (b) Fe–V<sub>O</sub>–Fe and (c) Mo–V<sub>O</sub>–Fe. (d) Lateral view of the structures of the \*OOH intermediates at Fe sites in KSFMO and in SFMO. Reproduced with permission from ref. 48. Copyright 2017, Royal Society of Chemistry. Schematic representation of octahedral distortion in (e) SrRuO<sub>3</sub> and (f) Sr<sub>0.9</sub>Na<sub>0.1</sub>RuO<sub>3</sub>. Fourier transform from Ru K-edge EXAFS signals of (g) SrRuO<sub>3</sub> and (h) Sr<sub>0.9</sub>Na<sub>0.1</sub>RuO<sub>3</sub> before and after OER cycles. Reproduced with permission from ref. 49. Copyright 2019, Nature Publishing Group.

and Mo–V<sub>O</sub>–Fe (Fig. 2c). When K atoms occupy A-site lattices, the V<sub>O</sub> formation energies of Fe–V<sub>O</sub>–Fe and Mo–V<sub>O</sub>–Fe in KSFMO are lower than those in SFMO because of charge compensation effects.<sup>68</sup> Interestingly, KSFMO will suffer a peculiar surface reconstruction upon V<sub>O</sub> formation along with Mo–V<sub>O</sub>–Fe. The Mo atom and surrounding O atoms undergo a structural rearrangement from an unsaturated octahedron to a tetrahedron MoO<sub>4</sub> moiety, and Fe atoms become highly under-coordinated (Fig. 2c). H-Bonds are formed during the reconstruction of the MoO<sub>4</sub> tetrahedron to stabilize \*OOH intermediates (Fig. 2d), which can accelerate the rate-determining step of the OER process. Meanwhile, the 3d orbital of the under-coordinated Fe cation, with a mixed Fe(III)/Fe(IV) character, has a strong overlap with the O 2p orbital, which is also beneficial for the ORR process.

The A-site doping of perovskite oxides with alkali metals also induces excellent cycling durability.<sup>49</sup> Pristine SrRuO<sub>3</sub>

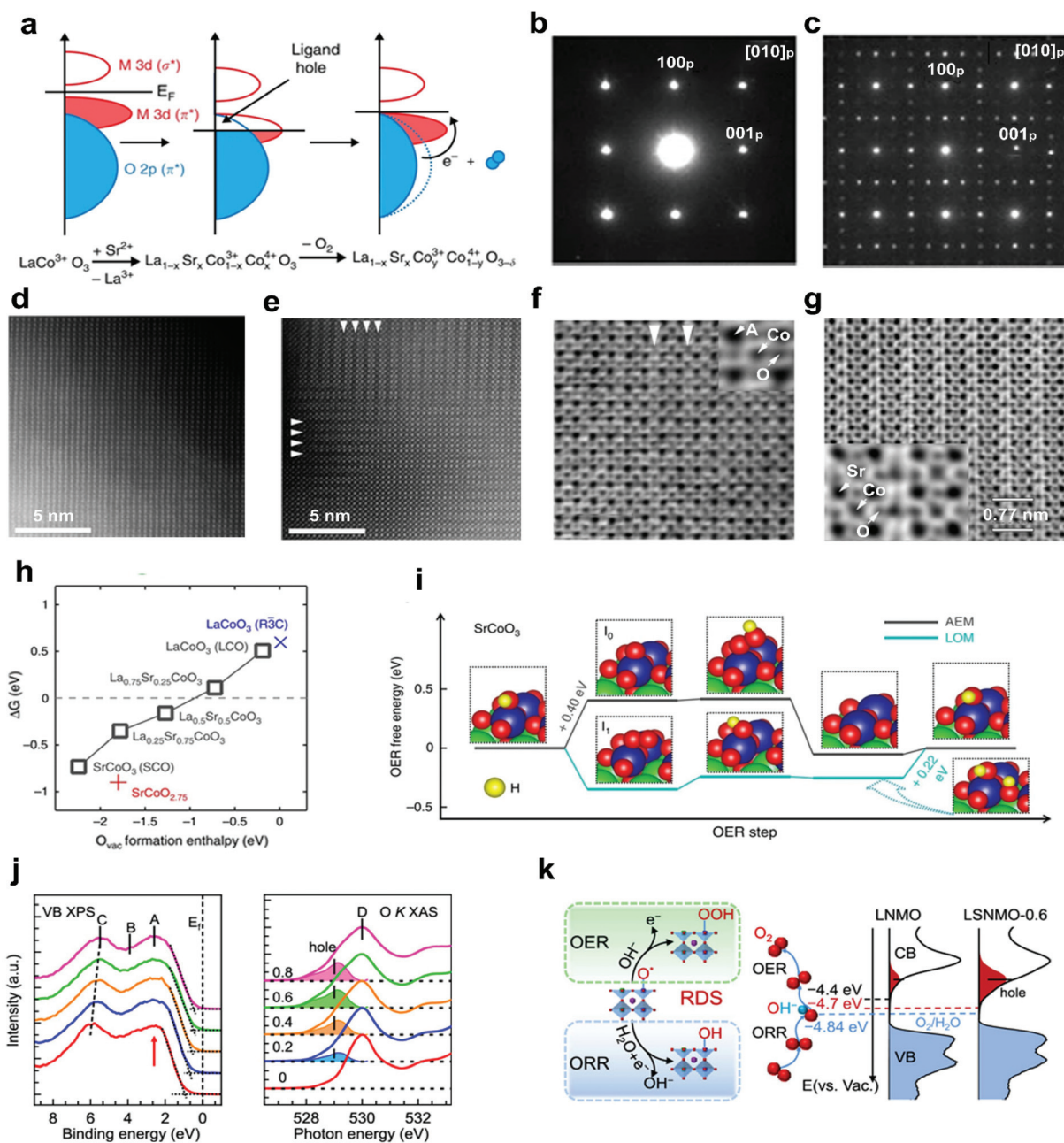
exhibits high specific OER activity but usually suffers from unsatisfactory durability, which is related to the distortion of Ru<sup>4+</sup>O<sub>6</sub> octahedra in SrRuO<sub>3</sub> (Fig. 2e). Upon Na<sup>+</sup> doping, Ru<sup>4+</sup> is slightly over-oxidized to Ru<sup>>4+</sup> because of charge compensation effects. Accordingly, the Ru<sup>>4+</sup>O<sub>6</sub> octahedra are more regular in Sr<sub>0.9</sub>Na<sub>0.1</sub>RuO<sub>3</sub> (Fig. 2f) due to decreased Jahn–Teller effects. Thus, a severely decreased Ru–O signal is observed for the cycled SrRuO<sub>3</sub> (Fig. 2g), indicating severe structural degradation. Conversely, similar signals are displayed in fresh and cycled Sr<sub>0.9</sub>Na<sub>0.1</sub>RuO<sub>3</sub> (Fig. 2h), confirming the high structural stability. Na locally increases the oxidation state of Ru from +4 to +5 and weakens the too strong adsorption energies of the OER intermediates. If Ru<sup>5+</sup> sites are instrumental for the development of SrRuO<sub>3</sub> perovskite oxide catalysts, other monovalent cations such as small radius Li<sup>+</sup> or large radius Cs<sup>+</sup> can be tested to ascertain whether they can also enhance the activity or the stability. This interesting

hypothesis would contribute to us for exploring other A-site alkali metal dopants.

## 2.2 A-site doping with alkaline-earth metals

In addition to alkali metal cations, bivalent alkaline-earth metal cations, such as  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ , have also been doped

into the A-site of perovskite oxides to improve the electrocatalytic efficiency. The substitution of bivalent  $\text{Sr}^{2+}$  for trivalent A-site cations usually causes a charge imbalance throughout the perovskite oxides.<sup>69</sup> This imbalance leads to the generation of oxygen vacancies, the modulation of oxidation states of the B-site transition metals, and the regulation of surface



**Fig. 3** (a) Schematic representation of the relationship between the oxygen vacancy concentration and Co–O bond covalency through  $\text{Sr}^{2+}$  doping. SAED patterns of (b)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  and (c)  $\text{SrCoO}_3$ . HAADF-STEM images of (d)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  and (e)  $\text{SrCoO}_3$ . ABF-STEM imaging of oxygen vacancy ordering in (f)  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_3$  and (g)  $\text{SrCoO}_3$ . (h)  $\Delta G$  (free energy difference between the LOM and AEM) versus the oxygen vacancy formation energy in perovskite oxides with different  $\text{Sr}^{2+}$  concentrations. (i) The OER free energy changes of the LOM and AEM on  $\text{SrCoO}_3$ . Reproduced with permission from ref. 67. Copyright 2014, Nature Publishing Group. (j) X-ray photoemission spectroscopy valence band and O K-edge XAS spectra of LSNMO with different  $\text{Sr}^{2+}$  concentration. (k) Left panel: rate-determining step of the OER and the ORR. Right panel: schematics diagram for the electronic structure near the Fermi level. Reproduced with permission from ref. 70. Copyright 2021, American Chemical Society.

morphology.<sup>67,70,71</sup> Ca<sup>2+</sup> doping can suppress surface segregation or induce a reformation into a stable structure, thereby yielding enhanced durability.<sup>50,72</sup>

In a recent study, aliovalent Sr<sup>2+</sup> cations were used to substitute La<sup>3+</sup> in LaMO<sub>3</sub> (M = Co, Fe, Ni, Mn), forming La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub>,<sup>67,71</sup> La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-δ</sub>,<sup>73</sup> La<sub>1-x</sub>Sr<sub>x</sub>NiO<sub>3-δ</sub>,<sup>51</sup> and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3-δ</sub>,<sup>74</sup> as efficient OER and ORR catalysts. For example, Stevenson and co-workers reported that the oxidation states of Co and the band overlap of Co 3d/O 2p are increased through Sr<sup>2+</sup> doping.<sup>67</sup> The formed ligand holes induce the release of lattice oxygen (Fig. 3a); therefore more oxygen vacancies will be created with the increased concentration of Sr<sup>2+</sup> in the La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> system. Compared with the crystal structures of low-level Sr<sup>2+</sup> doped La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3</sub> (Fig. 3b and d), obvious ordering of oxygen vacancies was observed in SrCoO<sub>3</sub> (Fig. 3c and e). The resulting layered ordered oxygen vacancies and atomic columns were directly observed in the high-level Sr<sup>2+</sup> doped La<sub>0.2</sub>Sr<sub>0.8</sub>CoO<sub>3</sub> (Fig. 3f) and SrCoO<sub>3</sub> (Fig. 3g), due to the decreased formation energy of oxygen vacancies as the Sr<sup>2+</sup> concentration increases (Fig. 3h). In addition, the oxygen evolution mechanism will transfer from the adsorbate evolution mechanism (AEM) to the lattice oxygen oxidation mechanism (LOM) with the increased Sr<sup>2+</sup> concentration. The OER occurs *via* the AEM on LaCoO<sub>3-δ</sub> and La<sub>0.75</sub>Sr<sub>0.25</sub>CoO<sub>3-δ</sub>, whereas on La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub> and SrCoO<sub>3-δ</sub>, it is mainly following the LOM mechanism (Fig. 3i).

The electronic structures of perovskite oxides can also be optimized by Sr<sup>2+</sup> doping. It was found that when Sr<sup>2+</sup> was doped into A sites, a shift of the whole valence band spectra towards the Fermi level (*E<sub>F</sub>*) and excess hole states were observed in La<sub>2-x</sub>Sr<sub>x</sub>NiMnO<sub>6</sub> (LSNMO) (Fig. 3j).<sup>70</sup> Such electronic modulation enhances the hybridization of O 2p with Ni/Mn 3d, further reducing the charge transfer barrier and improving the intrinsic ORR and OER activities (Fig. 3k). The Sr<sup>2+</sup> doping can also change the surface morphology due to the charge imbalance between Sr<sup>2+</sup> and trivalent A-site cations. The unbalanced charge distribution may cause the local structural disorder in the [BO<sub>6</sub>] octahedron, resulting in an increased specific surface area of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3-δ</sub> and a newly formed amorphous layer in La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub> with electrocatalytic activities.<sup>71,75</sup> A series of grain boundaries would form as an internal interface when amorphous layers and crystal layers are in direct contact with each other. The grain boundaries are considered as distinctive platforms to exhibit new physical and chemical properties.<sup>35</sup> This would be interesting to explore the effect of dopant-induced grain boundaries on perovskite oxide electrocatalytic performance.

The durability of perovskite oxides can also be significantly enhanced after doping with alkaline-earth cations. Perovskite oxide catalysts usually suffer from degradations during long-term operations because of the adverse changes in their crystal-structures and unstable surface-properties.<sup>76</sup> For instance, a decrease in the activity of Ba-containing perovskite oxides is related to the surface degradation and Ba leaching.<sup>77</sup> Luo *et al.* stabilized the crystal structure of PrBa<sub>0.85</sub>Ca<sub>0.15</sub>MnFeO<sub>5+δ</sub> (PBCMF) perovskite oxides by doping the A-site with Ca<sup>2+</sup>.<sup>50</sup> Its pristine Ca-free counterpart,

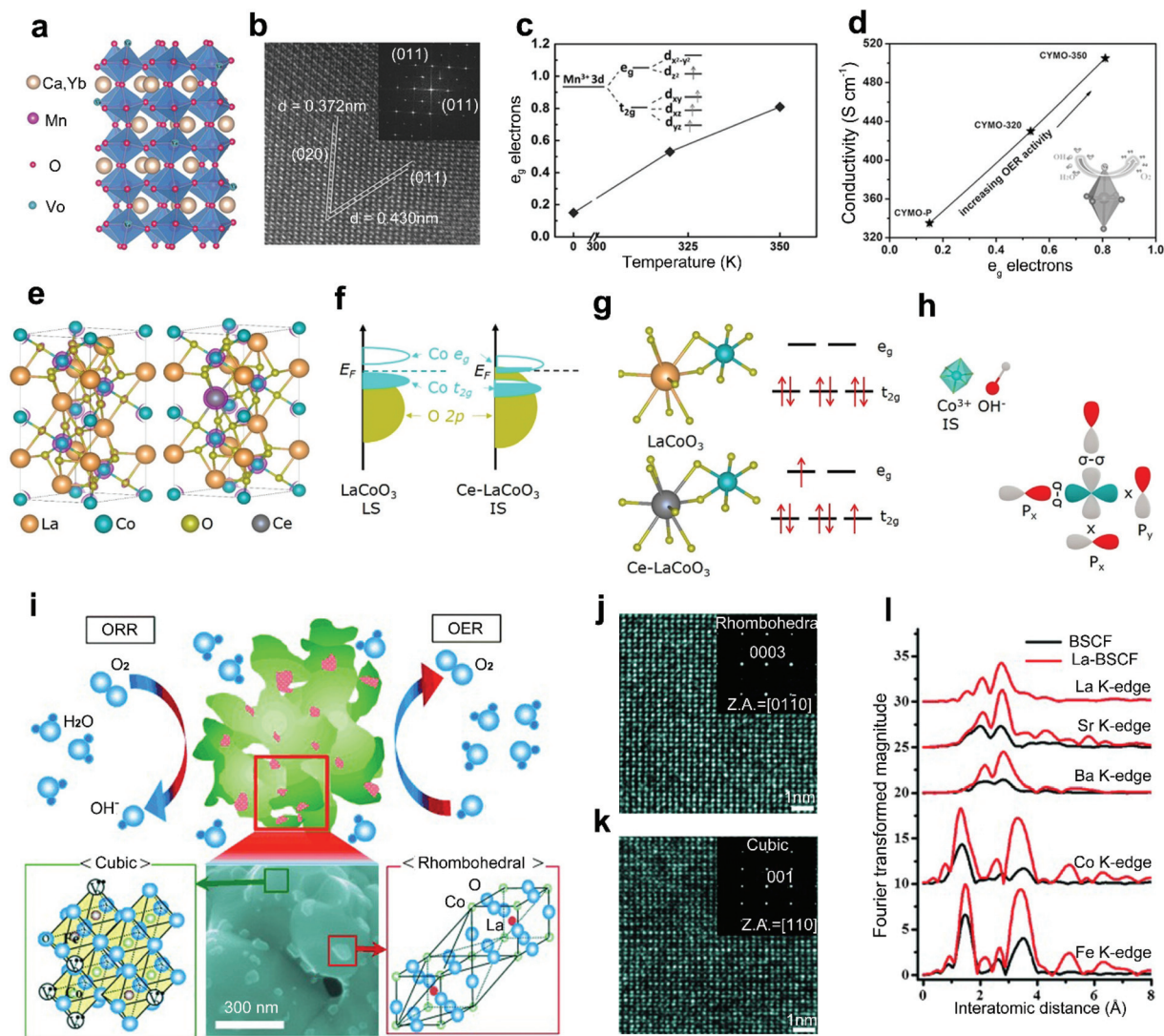
PrBaMnFeO<sub>5+δ</sub> (PBMF), suffered from an obvious degradation after a 1000-cycle test in the water oxidation reactions. A ~10 nm Ba-rich shell was observed on the surface of degraded PBMF. In contrast, all the elements were uniformly distributed across the entire region in PBCMF. The calculation results reveal that a small amount of Ca-doping can increase the corrosion resistance in perovskite oxides, preventing surface degradation and Ba leaching. In addition, the Ca doping was reported to induce a structural transformation from layered perovskite oxides to cubic perovskite oxides with improved structural stability, which can deliver a durable OER performance.<sup>77</sup>

### 2.3 A-site doping with rare-earth metals

The A-site doping with rare-earth metals will result in a large cation-size mismatch and charge imbalance between rare-earth metal dopants and A-site metal cations, which can improve the conductivity, optimize the B-site electron states, and construct an active secondary phase for improved activities of perovskite oxides.<sup>41,52</sup>

Xie *et al.*<sup>42</sup> reported a combined method of Yb<sup>3+</sup> doping and hydrogen treatment to improve the conductivity of CaMnO<sub>3</sub>. The Yb<sup>3+</sup> dopants with a higher valence compared to Ca<sup>2+</sup> can help to inject electrons to the perovskite oxides,<sup>78</sup> introducing suitable oxygen vacancies for improved conductivity (Fig. 4a). Meanwhile, a similar radius between Yb<sup>3+</sup> dopants and Ca<sup>2+</sup> maintains the orthorhombic phase crystal structure of Ca<sub>0.9</sub>Yb<sub>0.1</sub>MnO<sub>3-δ</sub> (Fig. 4b). The hydrogen treatment further improves the conductivity of CaMnO<sub>3</sub> by optimizing the e<sub>g</sub> electron filling status (Fig. 4c), showing a linear increasing relationship (Fig. 4d). The introduction of Yb also caused the degeneration of Mn e<sub>g</sub> orbitals into two sub-levels. The degeneration caused the elongation of Mn–O bonds owing to the Jahn–Teller effects (Fig. 4d). Such an elongation weakened the Mn–O covalent bond and facilitated the adsorption of oxygen intermediates. Therefore, significantly enhanced electrocatalytic activities were exhibited by the Yb-doped Ca<sub>0.9</sub>Yb<sub>0.1</sub>MnO<sub>3-δ</sub>.

In addition, rare-earth metal doping of the A-site in perovskite oxides can also contribute to the optimization of the electronic structure, leading to improved catalytic performance. Gao and co-workers reported an A-site doped LaCoO<sub>3</sub> with Ce<sup>3+</sup> as a robust OER and ORR catalyst (Fig. 4e).<sup>41</sup> In pristine LaCoO<sub>3</sub>, Co<sup>3+</sup> is stabilized in the low-spin state (LS: t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>0</sup>) and no obvious overlap is shown between the e<sub>g</sub> band of Co and O 2p states near the Fermi level (Fig. 4f). Differently, in the Ce-LaCoO<sub>3</sub>, the spin state of Co<sup>3+</sup> transitions from the LS to the steady intermediate-spin state (IS: t<sub>2g</sub><sup>5</sup>e<sub>g</sub><sup>1</sup>). The downshifted e<sub>g</sub> band toward the Fermi level enlarged the Co 3d/O 2p band overlap, resulting in efficient acceleration of electron transfer between active sites and oxygen intermediates (Fig. 4f). Accordingly, the electrons of Co<sup>3+</sup> in 3d orbital transition from t<sub>2g</sub> to e<sub>g</sub> (Fig. 4g). Then, improved OER activities under alkaline conditions can be achieved through a steady σ interaction between the activated e<sub>g</sub> orbitals of Co<sup>3+</sup> and the O 2p orbitals of OH<sup>-</sup> (Fig. 4h).<sup>79</sup>



**Fig. 4** (a) Crystal structure of  $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_{3-\delta}$  with oxygen vacancies. (b) High-resolution TEM (HRTEM) image of  $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_{3-\delta}$ . (c) Hydrogen treatment temperature versus average  $e_g$  electrons. (d) The average  $e_g$  electrons versus electrical conductivity. Reproduced with permission from ref. 42. Copyright 2015, Wiley-VCH. (e) The crystal structure of  $\text{LaCoO}_3$  and  $\text{Ce-LaCoO}_3$ . (f) Schematic representation of  $\text{Co } 3d$ – $\text{O } 2p$  overlap for  $\text{LaCoO}_3$  and  $\text{Ce-LaCoO}_3$ . (g) Schematic representation of the orbital splitting of  $\text{Co } 3d$  in  $\text{LaCoO}_3$  and  $\text{Ce-LaCoO}_3$ . (h) Schematic representation of the interaction between the  $\text{Co}^{3+}$  and  $\text{OH}^-$  in  $\text{Ce-LaCoO}_3$ . Reproduced with permission from ref. 41. Copyright 2020, Elsevier B.V. (i) Schematic representation of  $\text{La-BSCF}$  perovskite oxide catalysts. HRTEM images and corresponding SAED patterns of (j) rhombohedral  $\text{LaCoO}_3$  particles on the (k) cubic BSCF surface. (l) Radial distribution function for the all-atomic EXAFS spectra for BSCF and  $\text{La-BSCF}$ . Reproduced with permission from ref. 52. Copyright 2014, Wiley-VCH.

The surface morphology evolution, which would be induced by rare-earth metal doping in perovskite oxides, can also effectively affect the catalytic activities. Cho *et al.* reported a La-doped  $\text{La}_{0.3}(\text{Ba}_{0.5}\text{Sr}_{0.5})_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  ( $\text{La-BSCF}$ ) as a promising bifunctional perovskite catalyst for the ORR and OER.<sup>52</sup> Compared with the conventional powder morphology of BSCF,  $\text{La-BSCF}$  shows a flower-shaped morphology with particles on surfaces (Fig. 4i). The dynamic microstructure phenomenon is attributed to the charge imbalance by aliovalent  $\text{La}^{3+}$  doping, forming rhombohedral  $\text{LaCoO}_3$  (Fig. 4j) on the cubic BSCF surface (Fig. 4k). Additionally, the original  $\text{Co-O}$  bond in pristine BSCF is separated into two size-mismatched  $\text{Co-O}$  bonds (Fig. 4l). When compared with the BSCF, the  $\text{La-}$

BSCF with an excess active secondary phase provides more active sites for both the ORR and OER. For rhombohedral  $\text{LaCoO}_3$  and cubic BSCF perovskite oxides, these two crystal-line grains may form a grain boundary as an internal interface. This distinctive work provides an interesting idea to realize *in situ* formation of grain boundaries by heteroatom doping strategies.

### 3. B-site cation doping

In an ideal perovskite structure, transition metals occupying the  $[\text{BO}_6]$  octahedron can directly affect the electrocatalytic perform-

ance of perovskite oxides.<sup>80</sup> To design high-performance perovskite oxide catalysts, it is rational to introduce heteroatoms into B-site lattices of perovskite oxides. To comprehensively elucidate the types of B-site dopants in perovskite oxides, noble metals (*e.g.*, Ir, Ru, Pt, Ag),<sup>34,81–83</sup> non-noble metals (*e.g.*, Mn, Fe, Co, Ni),<sup>59,84–86</sup> and non-metals (*e.g.*, P, Si)<sup>58,87</sup> will be introduced in this section.

### 3.1 B-site doping with noble metals

Doping highly active noble metals into the B-site of perovskite oxides is a typical strategy used to design highly efficient electrocatalysts, such as Ag-BSCF,<sup>83</sup>  $\text{La}_{0.9}\text{Fe}_{0.92}\text{Ru}_{0.08}\text{O}_{3-\delta}$ ,<sup>88</sup>  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.1}\text{Ir}_{0.1}\text{O}_{3-\delta}$ ,<sup>89</sup> and  $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_{3-\delta}$ .<sup>82</sup> According to the work of Singhal *et al.*,<sup>90</sup> Ru-doped perovskite oxides

show higher current densities and more capacitive behaviors than their Ru-free counterparts and  $\text{RuO}_2$ . This originates from the excellent ionic activities of Ru in doped perovskite oxides, which are even higher than that of ionic Ru in the benchmark  $\text{RuO}_2$ . Hereafter, the positive effects of B-site doping with noble metals mainly stem from modulated electronic structures of original catalytic sites and generated new heteroatom catalytic sites.

Zou and co-workers reported Ir doped  $\text{SrTiO}_3$  (Ir-STO) with a remarkable OER activity in acidic media (Fig. 5a).<sup>81</sup> Pristine STO exhibits a negligible OER activity because the Ti 3d band is far from the Fermi level of STO (Fig. 5b). After the incorporation of Ir dopants, the electron density around Ti sites



**Fig. 5** (a) Schematic representation for the incorporation of Ir dopants in STO matrix. (b) DOS of Ir-STO and STO. (c) Ti 2p XPS spectra of Ir-STO and STO. (d) The charge density difference induced by oxygen adsorption on the Ti site in STO and Ir-STO. Reproduced with permission from ref. 81. Copyright 2019, Wiley-VCH. (e) HRTEM image and (f) corresponding fast Fourier transform (FFT) pattern of Ru-STO. (g) Schematic representation for top view of the charge distribution in Ru-STO. (h) Schematic representation of the super-exchange interaction in Ru-STO. (i) The oxygen non-stoichiometry and (j) electronic conductivity of STO and Ru-STO. (k) Schematic representation of the synergistic catalysis mechanism for an alkaline HER on Ru-STO. Reproduced with permission from ref. 34. Copyright 2020, Nature Publishing Group.

increases and the electrons are redistributed (Fig. 5c).<sup>91</sup> The density of states (DOS) of Ir-STO (Fig. 5b) also reveals an additional Ir electronic state crossing the Fermi level, and the Ti 3d band and O 2p band are closer to the Fermi level compared with STO. In this regard, the adsorption of oxygen intermediates on the Ti site is strengthened in the potential-determining step (Fig. 5d). This Ir doping strategy enables the possibility of designing high catalytic activity electrocatalysts for the OER under acid conditions, with a smaller amount of precious metals than their IrO<sub>2</sub> counterpart.

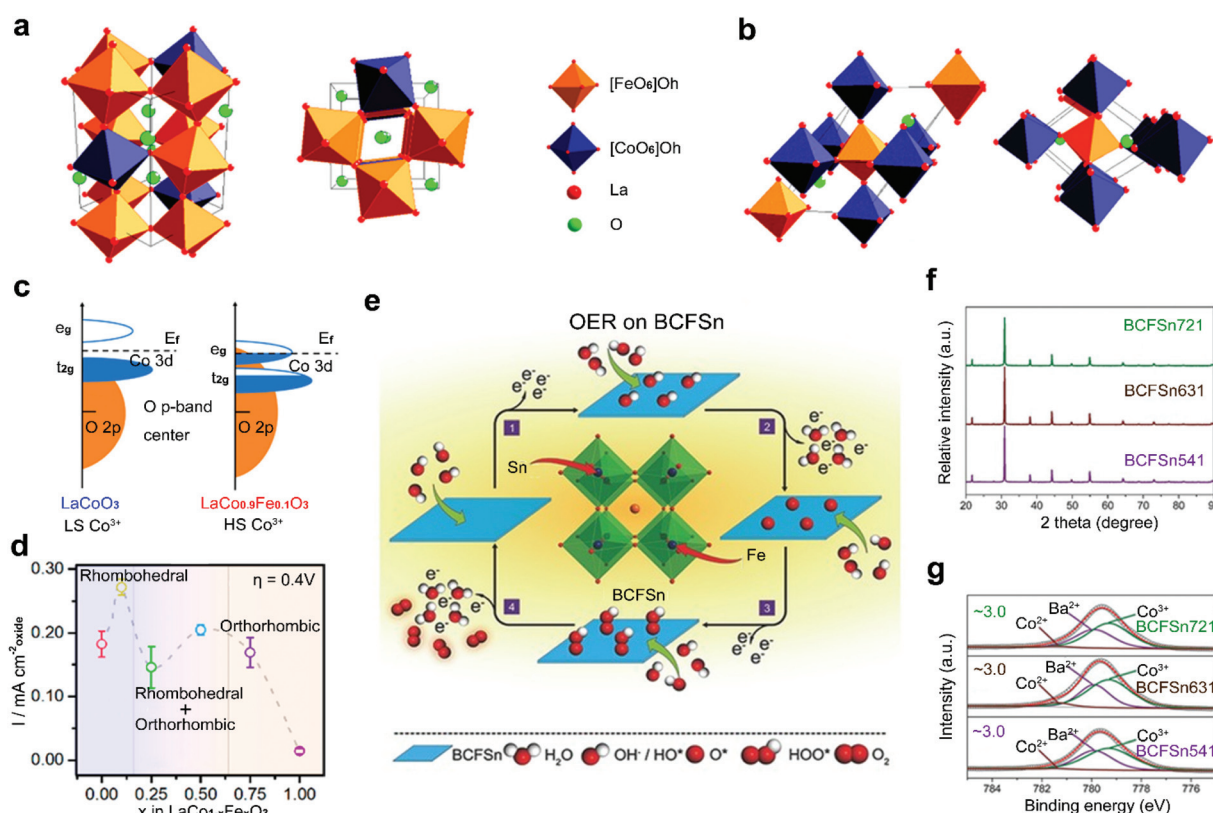
Dai and co-workers introduced a Ru-doped single-phase SrTiO<sub>3</sub>, SrTi<sub>0.7</sub>Ru<sub>0.3</sub>O<sub>3-δ</sub> (Ru-STO), with ultrafast HER performance in alkaline media (Fig. 5e and f).<sup>34</sup> The incorporation of Ru dopants into STO leads to a charge redistribution between the neighbouring Ti and Ru ions (Ti<sup>4+</sup> + Ru<sup>4+</sup> → Ti<sup>3+</sup> + Ru<sup>5+</sup>) (Fig. 5g), resulting in an unusual super-exchange interaction between adjacent Ti<sup>3+</sup> (with a 3d<sup>1</sup> configuration) and doped Ru<sup>5+</sup> (with a 4d<sup>3</sup> configuration) (Fig. 5h).<sup>43</sup> In addition, oxygen vacancies are generated in the Ru-STO (Fig. 5i), which enhances the electrical conductivity (Fig. 5j) and contributes to exceptional catalytic activities. Density functional theory (DFT) calculations further reveal that the excellent activities are primarily attributed to a unique synergistic effect among the activated Ti sites, doped Ru sites and increased oxygen

sites, which facilitate the water dissociation, enhance the OH\* desorption, and promote the optimal H\* adsorption and H<sub>2</sub> desorption, respectively (Fig. 5k).

Though B-site doping of perovskite oxides with noble metals is promising for achieving fast kinetics and high current density with a low overpotential, the large-scale commercial applications are restricted by the high cost and resource scarcity of the noble metals.<sup>54</sup> Besides, drastic structural instability during long-term operations has been observed, due to the dissolution of the formed noble metal oxides (RuO<sub>x</sub> and IrO<sub>x</sub>) on the surfaces of doped perovskite oxides.<sup>49</sup>

### 3.2 B-site doping with non-noble metals

Non-noble transition metals (*e.g.*, Fe, Co, Ni, Mn) have been intensively investigated as B-site dopants because of their common merits of low cost and Earth-abundance.<sup>84–86</sup> Some non-noble transition metals also have their specific merits. Mn-incorporated materials usually work well in the ORR,<sup>52,92</sup> Co/Ni-doped materials show high OER activities,<sup>93–95</sup> and Fe-based materials are relatively environmentally friendly.<sup>96,97</sup> Therefore, it is highly desirable to dope these non-noble transition metals into perovskite oxides for the development of large-scale energy production.



**Fig. 6** Schematic representation for perovskite oxide structures with (a) distorted rhombohedral structure and (b) orthorhombic structure. (c) Schematic representation of Co 3d–O 2p overlap for LaCoO<sub>3</sub> and LaCo<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub>. (d) Specific current density and corresponding structure for LaCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> at an overpotential of 0.4 V versus RHE. Reproduced with permission from ref. 85. Copyright 2017, American Chemical Society. (e) Schematic representation of OER process of BCFSn perovskite oxides. (f) XRD patterns of BCFSn perovskite oxides. (g) High-resolution XPS spectra of Co 2p<sub>3/2</sub> for BCFSn perovskite oxides. Reproduced with permission from ref. 103. Copyright 2016, Wiley-VCH.

Perovskite oxides are found to be more active toward the OER when a relatively small amount of Fe is doped into the B-site.<sup>98,99</sup> Xu and co-workers analysed the role of Fe-doping in perovskite oxide catalysts in the OER and found that the structure of  $\text{LaCoO}_3$  is changed with the incorporated content of Fe. The  $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$  with a low concentration of doped Fe corresponds to a rhombohedral structure (Fig. 6a).<sup>100</sup> When the concentration of doped Fe increases, the  $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$  transitions from the rhombohedral phase to an orthorhombic phase (Fig. 6b). The phase change leads to the spin state transition of  $\text{Co}^{3+}$  from LS to HS and results in enhanced hybridization between Co 3d states and O 2p states (Fig. 6c). At an optimized concentration of doped Fe, remarkably enhanced OER activity is achieved (Fig. 6d). The doped Fe can also extend the potential range of thermodynamic metastability and improve the stability of the perovskite oxide structures through the formation of an oxy(hydroxide) layer on surfaces under OER conditions,<sup>101</sup> which is the actual active layer for the OER.<sup>102</sup>

Two kinds of transition metals can also be co-doped into the B-site of perovskite oxides. Shao *et al.* reported a co-doping

strategy by introducing Fe and Sn into the B-site of inert  $\text{BaCoO}_{3-\delta}$  to design highly active  $\text{BaCo}_{0.9-x}\text{Fe}_x\text{Sn}_{0.1}\text{O}_{3-\delta}$  (BCFSn) as OER catalysts (Fig. 6e).<sup>103</sup> The introduction of both Fe and Sn elements can not only optimize the  $\text{OH}^-$  adsorption capability,  $\text{O}_2$  desorption capability, average metal–oxygen bond energy and electrical conductivity, but also stabilize the cubic-phase structure (Fig. 6f) and the oxidation state of surface Co atoms (Fig. 6g). Thus, a four-electron transfer pathway for the OER is greatly boosted in BCFSn. Some other co-doped perovskite oxides have also been developed, such as Co/Ni co-doped  $\text{Sr}_2\text{FeMoO}_{6-\delta}$ ,<sup>104</sup> Cu/Co co-doped  $\text{LaMnO}_{3-\delta}$ ,<sup>105</sup> and Cu/Fe co-doped  $\text{LaNiO}_{3-\delta}$ .<sup>106</sup> The optimized electronic structure of active sites and increased amount of oxygen vacancies are found in these co-doped perovskite oxides with improved catalytic activities.

### 3.3 B-site doping with non-metals

B-site doping of perovskite oxides with non-metal elements provides another attractive way to improve the electrocatalytic activities. Non-metal elemental dopants are inert by them-



**Fig. 7** (a) Schematic representation of the crystal structure of Si-SCO. (b) HRTEM image of Si-SCO and the corresponding FFT pattern. (c) Schematic representation of the AEM and LOM reaction pathways on Si-SCO. Reproduced with permission from ref. 58. Copyright 2020, Nature Publishing Group. (d) HRTEM images of surface regions of P-SCO (d) before and (e) after 1000 cycles. (f) Schematic representation of the main origin of the OER activation in the SCP sample. Reproduced with permission from ref. 57. Copyright 2016, Wiley-VCH. (g) Mössbauer spectrum of LFO and P-LFO. (h) Schematic representation of Fe 3d orbit degeneration. Reproduced with permission from ref. 87. Copyright 2018, Elsevier B.V.

selves towards electrocatalysis, such as silicon (Si) and phosphorus (P).<sup>57,58,87,107</sup> However, the non-metal elemental doping of perovskite oxides usually results in additional reaction pathways, favorable structural transitions, boosting electrical conductivities and optimized active sites, which are beneficial to efficient electrocatalysis.

Si doping can influence the catalytic performance of perovskite oxides through diverse ways, such as activation of additional reaction pathways, optimization of surface structures, and creation of oxygen vacancies. Shao's group introduced Si to the B-site of SrCoO<sub>3</sub> (Fig. 7a) to form a tetragonal-phase Si-SrCoO<sub>3</sub> (Si-SrCO) (Fig. 7b).<sup>58</sup> The pH-dependence of the OER kinetics and almost unchanged  $e_g$  filling of Co in Si-SrCO prove that the boosted electrocatalytic activities should be attributed to an activated LOM mechanism (Fig. 7c) instead of the AEM.<sup>108</sup> Besides, the increased pseudocapacitive behaviors of Si-SrCO also indicate the involvement of lattice oxygen redox during the OER. The OER enhancement can also result from structural transition upon non-metal doping of perovskite oxides.<sup>58</sup> A Si-doped SrFeO<sub>3- $\delta$</sub>  (Si-SFO) is designed and shows an approximately three-fold increase in OER activity relative to SrFeO<sub>3- $\delta$</sub> .<sup>107</sup> This obviously enhanced OER activity can be

ascribed to the structural transition from tetragonal to cubic phase originating from Si doping, accompanying the generation of abundant oxygen vacancies and further acceleration of charge transfer.

The introduction of P elements into perovskite oxides can affect the electrochemical surface areas and B-site electronic structures of perovskite oxides. For example, an increase in OER activities is observed for P-doped SrCoO<sub>3</sub> (P-SCO) after a 1000-cycle test.<sup>57</sup> This increase is due to the formation of an amorphous layer with a thickness of 1–2 nm on the surfaces of P-SCO during the durability tests (Fig. 7d and e). The surface amorphization, associated with the leaching of A-site Sr<sup>2+</sup>, can lead to the exposure of active B sites and oxygen vacancies on the perovskite surface (Fig. 7f) and thus increase the electrochemical surface areas. Afterwards, Liu *et al.* found that compared with the pristine LaFeO<sub>3- $\delta$</sub>  (LFO), P-doped LaFeO<sub>3- $\delta$</sub>  (P-LFO) shows almost double times higher ORR activities under alkaline conditions.<sup>87</sup> Upon the incorporation of P, the valence states of partial Fe-sites increase from Fe<sup>3+</sup> to Fe<sup>4+</sup> (Fig. 7g). In particular, the generation of Fe<sup>4+</sup> results in the degeneration of the Fe 3d orbital (Fig. 7h). With the coexistence of Fe<sup>4+</sup>/Fe<sup>3+</sup>/Fe<sup>2+</sup>, the  $e_g$  electron filling is optimized



**Fig. 8** (a) HRTEM image of LBSCOF. (b) Schematic representation of the perovskite oxide structure and featured [CoO<sub>6- $\delta$</sub> ] polyhedron. (c) XPS spectra of O 1s for LBSCOF and LBSCO. Reproduced with permission from ref. 60. Copyright 2018, Elsevier Inc. (d) Schematic representation for optimized atomic structures. (e) Schematic representation of the evolution of the IS state and the transition of electrons from  $t_{2g}$  to  $e_g$  orbital. Reproduced with permission from ref. 109. Copyright 2020, American Chemical Society. (f) ABF-STEM image of N-LCO. (g) Spin density distribution and electronic configuration of LCO and N-LCO. (h) Schematic representation of orbital bonding. (i) Illustration diagram of the four-step process of the OER. Reproduced with permission from ref. 62. Copyright 2021, American Chemical Society.

close to 1. What's more, the incorporation of P cations can also generate rich oxygen vacancies. With the optimized  $e_g$  orbital filling and abundant oxygen vacancies, P-LFO possesses enhanced ORR catalytic activity.

## 4. O-site anion doping

In addition to the above cation doping, replacement of partial oxygen anions in the perovskite oxides by other non-metal heteroatom anions has also been explored to improve the activities of perovskite oxides, such as F,<sup>33,60</sup> S,<sup>61,109</sup> N,<sup>62</sup> and Cl.<sup>110</sup> The introduction of anions with different electronegativities or valences into the perovskite matrix can decrease the formation energy of oxygen vacancies, modify the electronic state and induce surface structure transformation of perovs-

kite, and therefore contribute to the manipulation of catalytic performance.

F is a widely used dopant to improve the electrocatalytic performance of perovskite oxides. Due to a less negative valence of  $-1$  than  $-2$  of O anions, the substitution of O with F induces a transformation from the  $[\text{CoO}_6]$  octahedral structure to  $[\text{CoO}_5\text{F}]$  and  $[\text{CoO}_5]$  in cubic F-doped  $\text{La}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$  and  $\text{La}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25}\text{CoO}_{3-\delta}\text{F}_{0.1}$  (LBSCOF) (Fig. 8a).<sup>60</sup> The formed octahedral  $[\text{CoO}_5\text{F}]$  symmetry and square pyramidal  $[\text{CoO}_5]$  symmetry lead to a reconfiguration of Co in the  $e_g$  and  $t_{2g}$  orbitals (Fig. 8b). Besides, owing to the larger electronegativity of  $\text{F}^-$  than that of  $\text{O}^{2-}$ , the coulombic force between B-site cations and O can be weakened upon F doping. Thus, a lower formation energy of the oxygen vacancy is needed in LBSCOF than that in pristine  $\text{La}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$  (LBSCO). More content of active oxygen species is observed in LBSCOF than LBSCO (Fig. 8c). The opti-



**Fig. 9** (a) Schematic representation of epitaxial growth of Sr&Fe-LNO perovskite oxide thin films on a  $\text{SrTiO}_3$  substrate. (b) XPS valence band spectrum and (c) schematic representation of the electronic coupling between the  $\text{Ni}^{3+}$  and  $\text{Fe}^{3+}$  in LNO and between the  $\text{Ni}^{3+}$  and  $\text{Fe}^{4+}$  in Sr&Fe-LNO, respectively. (d) The comparison of the occupied DOS (VB) and unoccupied DOS (CB) near  $E_f$  for LNO and Sr&Fe-LNO on an absolute energy scale. Reproduced with permission from ref. 64. Copyright 2021, Wiley-VCH. (e) The  $e_g$  orbital filling of different perovskite oxides and OER activity as a function of  $\text{Ni}^{3+}/\text{Ni}^{2+}$  rate. Reproduced with permission from ref. 63. Copyright 2019, Frontiers Media S.A. (f) Schematic representation of crystal structure of Ni-LFO and Ni&Se-LFO. DOS of (g) LFO, (h) Ni-LFO, and (i) Ni&Se-LFO, respectively. Reproduced with permission from ref. 47. Copyright 2020, American Chemical Society.

mized electronic orbital of Co and formed active oxygen species greatly promote the water-splitting reactions. As an element of the halogen group, Cl anions have the same  $-1$  valence but lower electronegativity than F anions. Wang *et al.* experimentally investigated the role of Cl dopants. The enhanced OER activity of  $\text{LaFeO}_{2.9-\delta}\text{Cl}_{0.1}$  was ascribed to the fact that the Cl dopants enriched abundant oxygen vacancies, increased the electrical conductivity and enhanced the Fe–O covalency.<sup>110</sup>

S is another efficient dopant for the O-site doping of perovskite oxides. S anions have the same  $-2$  valence as O anions, but larger ionic radius than O anions. Therefore, the B–O bond lengths of  $[\text{BO}_6]$  octahedra are changed and oxygen vacancies are formed after doping S into the O-site. These phenomena are observed in a recently reported S-doped  $\text{LaCoO}_3$  (S-LCO).<sup>109</sup> During the *in situ* vapor–solid reaction process, the sulfur atoms react with  $\text{LaCoO}_3$  perovskite oxides and are reduced into sulfur anions. The sulfur anions are anchored on the O sites and a distorted  $[\text{BO}_6]$  octahedral structure is formed (Fig. 8d). The distorted structure induces the spin state transition of Co from low spin to intermediate spin in S-LCO (Fig. 8e). Compared with pristine LCO, S-LCO shows greatly improved activities for both the OER and ORR under alkaline conditions. The influences of S dopants during the electrocatalytic process are also investigated by DFT calculations. Theoretical simulation reveals an elongated O=O double bond in S doped perovskite oxides during the ORR process.<sup>61</sup> The easier  $\text{O}_2$  cleavage indicates that S doping can

endow perovskite oxides with an optimal electronic structure and surface adsorption feature for ORR catalysis.

With a low electronegativity and a high level of the 2p orbital, N atoms can exchange electrons in 2p orbitals with 3d orbitals of B-site active cations.<sup>111</sup> Recently, Gao and co-workers reported an N-doped  $\text{LaCoO}_3$  (N-LCO) with enhanced oxygen catalytic activities (Fig. 8f).<sup>62</sup> In typical  $\text{LaCoO}_3$ , the Co cations show a low spin state with  $e_g$  occupancy of  $\sim 0$ . In contrast, in the N-LCO, N provides Co with an additional electron through the N–Co bond, resulting in a moderate  $e_g$  occupancy of  $\sim 1$  for the Co cations (Fig. 8g). Then, the interaction between the 3d orbital of  $\text{Co}^{3+}$  and the 2p orbital of surface-adsorbed O intermediates is promoted (Fig. 8h). Eventually, a four-step process of the OER is greatly accelerated (Fig. 8i).

## 5. Dual-site doping

Although single-site doping of heteroatoms into  $\text{ABO}_3$  perovskite oxides has been intensively studied, the optimized performance is still somehow far from satisfaction. Recently, a dual-site doping strategy has been explored by doping diverse heteroatom dopants into A and B sites or B and O sites of perovskite oxides. A synergistic promotion is supposed to be achieved among multi-active sites induced by dual-site doping.<sup>47,63,64</sup>

Zhang *et al.* doped Sr and Fe heteroatoms into A and B sites of  $\text{LaNiO}_3$  (LNO), respectively (Fig. 9a).<sup>64</sup> Single-site doping of

**Table 1** Catalytic performance comparisons of doped and pristine perovskite oxide catalysts

| Composition engineering | Dopants | Catalysts<br>Doped/pristine materials  | Catalytic performance |                  |                  | Ref. |
|-------------------------|---------|--|-----------------------|------------------|------------------|------|
|                         |         |  | HER <sup>a</sup>      | OER <sup>b</sup> | ORR <sup>c</sup> |      |
| A site doping           | Na      | $\text{Sr}_{0.95}\text{Na}_{0.05}\text{RuO}_3/\text{SrRuO}_3$  |                       | 0.16/0.19        |                  | 49   |
|                         | Sr      | $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3/\text{LaCoO}_3$  |                       | 0.41/0.44        |                  | 67   |
|                         | Ce      | $\text{Ce-LaCoO}_3/\text{LaCoO}_3$   |                       | 0.41/0.65        | 0.68/0.45        | 41   |
|                         | La      | $\text{La}_{0.3}(\text{Ba}_{0.5}\text{Sr}_{0.5})_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$   |                       | 0.32/0.44        |                  | 52   |
|                         | Sr      | $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{LaCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$                                    |                       | 0.45/0.56        |                  | 71   |
| B site doping           | Sr      | $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}/\text{LaFeO}_3$   |                       | 0.24/0.35        |                  | 73   |
|                         | Ti      | $\text{SrTi}_{0.7}\text{Ru}_{0.3}\text{O}_{3-\delta}/\text{SrRuO}_{3-\delta}$  | 0.05/0.09             |                  |                  | 33   |
|                         | Ir      | $\text{SrTi}_{0.67}\text{Ir}_{0.33}\text{O}_3/\text{SrTiO}_3$  |                       | 0.24/0.32        |                  | 81   |
|                         | Pt      | $\text{LaCo}_{0.94}\text{Pt}_{0.06}\text{O}_{3-\delta}/\text{LaCoO}_{3-\delta}$  | 0.29/0.44             | 0.454/0.541      |                  | 82   |
|                         | Ag      | $\text{Ag-Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$     |                       | 0.44/0.51        |                  | 83   |
|                         | Si      | $\text{Si-SrCoO}_{3-\delta}/\text{SrCoO}_{3-\delta}$   |                       | 0.417/0.488      |                  | 58   |
|                         | Co      | $\text{LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3/\text{LaFeO}_3$  |                       | 0.34/0.36        |                  | 59   |
|                         | Fe      | $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3/\text{La}_{0.58}\text{Sr}_{0.4}\text{CoO}_3$  |                       | 0.422/0.490      |                  | 92   |
|                         | Ru      | $\text{SrCo}_{0.9}\text{Ru}_{0.1}\text{O}_{3-\delta}/\text{SrCoO}_{3-\delta}$  |                       | 0.36/0.44        |                  | 43   |
|                         | Sn/Fe   | $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Sn}_{0.1}\text{O}_{3-\delta}/\text{BaCoO}_{3-\delta}$   |                       | 0.42/0.45        |                  | 103  |
| O site doping           | S       | S doped $\text{LaCoO}_3/\text{LaCoO}_3$  |                       | 0.364/0.473      |                  | 109  |
|                         | Cl      | $\text{LaFeO}_{2.9-\delta}\text{Cl}_{0.1}/\text{LaFeO}_3$  |                       | 0.47/0.51        |                  | 110  |
|                         | F       | $\text{F-Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$      |                       | 0.28/0.34        |                  | 33   |
|                         | F       | $\text{La}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25}\text{Co}_{0.2}\text{O}_{2.9-\delta}\text{F}_{0.1}/\text{La}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ | 0.17/0.22             | 0.39/0.43        |                  | 60   |
|                         | S       | S doped $\text{CaMnO}_3/\text{CaMnO}_3$  |                       | 0.47/0.62        | 0.72/0.68        | 61   |
|                         | N       | N doped $\text{LaCoO}_3/\text{LaCoO}_3$  |                       | 0.37/0.57        | 0.63/0.62        | 62   |
| Dual site doping        | Se, Ni  | Se, Ni doped $\text{LaFeO}_3/\text{LaFeO}_3$   |                       | 0.307/0.330      |                  | 47   |
|                         | Sr, Fe  | $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ni}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{LaNiO}_3$  |                       | 0.320/0.473      |                  | 63   |
|                         | Sr, Fe  | Sr, Fe doped $\text{LaNiO}_3/\text{LaNiO}_3$   |                       | 0.33/0.49        |                  | 64   |

<sup>a</sup> The overpotential at a current density of  $10 \text{ mA cm}^{-2}$  (V vs. RHE). <sup>b</sup> The overpotential at a current density of  $10 \text{ mA cm}^{-2}$  (V vs. RHE). <sup>c</sup> Half-wave potential (V vs. RHE).

LNO with Fe (Fe-LNO) only shows a  $\text{Fe}^{3+}$  oxidation state with a shift of the whole valence band (VB) photoemission spectrum of Fe-LNO away from  $E_f$  (Fig. 9b). However, the Sr and Fe dual-site doped LNO (Sr&Fe-LNO) shows a promoted Fe state from +3 to +4. The activated  $\text{Fe}^{4+}$  states induce an inverse shift of the whole VB spectrum back close to  $E_f$  (Fig. 9b). The presence of  $\text{Fe}^{4+}$  can also reduce the electron–electron repulsion from bridging O (Fig. 9c) and facilitate the generation of active  $\text{Ni}^{4+}$  states. Besides, a reduced energy barrier of electron transfer is achieved for the Sr&Fe-LNO compared with LNO (Fig. 9d). Consequently, a six times higher current density is obtained for the Sr&Fe-LNO than that of LNO and Fe-LNO. In another report, by regulating the proportion of Sr and Fe nitrate precursors, an optimal  $e_g$ -filling value of 1.2 is achieved through the dual-site doping with Sr and Fe (Fig. 9e).<sup>63</sup>

Dual-site doped  $\text{LaFeO}_3$  with Ni and Se into B and O sites, respectively, is explored as a robust OER catalyst (Fig. 9f).<sup>47</sup> The adsorption energies of oxygenated species on Fe sites are stronger than those of Ni sites.<sup>112</sup> The substitution of the B-site Fe by adding different amounts of nickel salts into precursor solutions can optimize the adsorption of oxygen intermediates during the OER process. Furthermore, a mixture of Se powder and Ni single-site doped LFO (Ni-LFO) is annealed under an argon atmosphere. Se atoms are doped into O sites and lead to the formation of tremendous oxygen vacancies. The electron-occupied states crossing the Fermi level are increased in Ni and Se dual-site doped LFO (Ni&Se-LFO) compared to Ni-LFO and LFO (Fig. 9g–i). Finally, both experimental results and theoretical calculations demonstrate that Ni&Se-LFO shows superior OER catalytic activities to single-doped Ni-LFO and LFO.

## 6. Conclusion and perspective

This review summarizes the recent advances in the heteroatom doping of perovskite oxides. The catalytic performances of current doped perovskite oxide catalysts are listed in Table 1. The types of doping were classified in terms of the categories of the doping sites in  $\text{ABO}_3$ -type perovskite oxide structures, including A-site doping, B-site doping, O-site doping, and dual-site doping. Based on these doping strategies, the electrocatalytic activities of perovskite oxides can be effectively enhanced by the optimization of active site states, introduction of oxygen vacancies, regulation of surface morphologies, and surface reconstruction. Nevertheless, there are also many challenges that deserve further investigation.

Most of the present research studies focus on single-site doping of perovskite oxides with heteroatoms. Compared with single-site doping, dual-site doping is supposed to show higher energy-efficiency for perovskite oxides.<sup>47,63,64</sup> Available examples mentioned above have demonstrated that dual-site doping could introduce more remarkable influences on the electrocatalytic behaviors of perovskite oxides, thus worthy of our in-depth study. Current research studies have focused on doping different types of heteroatoms into multiple sites.

However, there are enormous possible combinations of heteroatom dopants in perovskite oxide materials, which intensively hinder our efficient screening in the search for a combination with optimal catalytic properties. Thus, for a dual-site doping strategy, how to select the optimal heteroatom dopants remains a huge challenge. Recently, S has been doped into both B sites and O sites of perovskite oxides simultaneously, due to its relatively moderate electronegativity.<sup>57,61</sup> It is highly possible that some other non-metal elements with similar electronegativity could also function as both an electron acceptor and an electron donor, showing great potential of multi-site dopants for next-generation doping strategies.

While searching for optimal doping strategies, advanced *in situ* techniques should be considered to clarify the dynamic variation of dopant precursors during the doping process and real-time interaction between the doped heteroatoms and active sites during catalytic reactions. For example, *in situ* scanning transmission electron microscopy (STEM) characterization can facilitate our accurate determination of the locations of heteroatoms and record of atomic displacements of active sites.<sup>35</sup> Operando X-ray absorption spectral (XAS) measurements can help to understand the functional role of doped heteroatoms in perovskite oxides during the catalytic reactions.<sup>101</sup> *In situ* Raman technology can capture the dynamic surface reconstruction and facilitate our understanding of the surface catalytic mechanism during the evolution of the active phase.<sup>113</sup> Currently, Bao's group discovered the reversible exsolution and dissolution of metal nanoparticles in Co-doped  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (Co-SFMC) perovskite oxides using advanced *in situ* techniques.<sup>114</sup> *In situ* XRD and STEM revealed that the doped Co was exsolved from the parent perovskite and facilitated the generation of CoFe alloy nanoparticles on the surface of Co-SFMC, leading to enhanced  $\text{CO}_2$  electrolysis performance. These *operando* techniques visually demonstrate the structural evolution of electrocatalysts and provide us with more detailed research to understand the specific behavior of heteroatoms for catalyst synthesis and reaction processes.

The current research studies of doped perovskite oxide electrocatalysts are mainly focused on the HER, OER, and ORR. Currently, perovskite oxides have been demonstrated with activities toward the NRR under ambient conditions.<sup>30,115</sup> The activities are mainly attributed to the favourable merits produced by the oxygen vacancies, which could have originated from heteroatom doping. Indeed, Bi's group improved the NRR catalytic performance of heteroatom-doped perovskite oxides.<sup>116</sup> They found that A-site Sr doping can create abundant oxygen vacancies in Sr-doped LFO ( $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ ). The enriched oxygen vacancies weaken the  $\text{N}\equiv\text{N}$  triple bonds and accelerate the formation of  $\text{N}-\text{H}$  bonds. Considering the high composition tunability of perovskite oxides and various types of heteroatom dopants, we anticipate that perovskite oxide catalysts doped with specific and optimized heteroatoms may be applied to other catalytic fields.

Overall, perovskite oxide-based electrocatalysts will indeed have a promising outlook in the electrocatalytic field, owing to

their multiple advantages of Earth abundance, low cost, structural diversity and high efficiency. With the gradually optimized synthetic strategies and advanced *in situ* techniques, the role of heteroatom dopants will be further understood at the atomic level. The heteroatom doping strategy could pave the way for the development of practical perovskite oxide catalysts for widespread applications in energy-related catalysis fields.

## Conflicts of interest

There are no conflicts to declare.

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