

The role of nonmetallic ion substitution in perovskite LaCoO_3 for improved oxygen evolution reaction activity

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ABSTRACT

Transition metal perovskite (ABO_3) is an emerging type of oxygen evolution reaction (OER) electrocatalyst that shows reasonably good activity and moderate stability. Although efforts have been made to improve perovskite's OER performance by various element substitution at A/B-site, the influence of ion, particularly non-metallic ion, substitutions on the OER mechanism are rarely studied. More and more evidence has shown that the metal-center theory has failed to explain lots of OER-related phenomena. Therefore, it is urgent to understand how the cation and anion sites in perovskite determine OER performance. Here, we used a Fe and P co-doped LaCoO_3 as a model system to explore the influence of substitution in perovskite by combining *operando/ex-situ* X-ray characterization and density functional theory (DFT). We observed enhanced OER catalytic activities in co-doped materials, which are attributed to the stronger transition-metal-oxygen-bonding-covalency (TMOBC). The detailed analyses by O K-edge XAS, electrochemical performance, and DFT suggest that the hybridization between O 2p and transition metal 3d e_g orbitals could be a more credible descriptor of perovskite for OER, which is the combination of e_g orbital theory and TMOBC theory. The finding in our work provides insights into the OER catalysis mechanism on metal oxides, which could guide new design of cost-effective oxide electrocatalysts.

1. Introduction

Developing sustainable energy conversion and storage techniques is key to combatting climate change and responding to its harmful effects [1–3]. A promising solution is the use of electrochemical energy conversion devices such as electrolyzers to split water and produce hydrogen, which can be stored and used as a green energy resource, thereby promoting the so-called “hydrogen economy” [4,5]. Water splitting consists of two main electrochemical reactions, namely hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), occurring at the cathode and the anode, respectively. The OER is a four-electron process that is more challenging, compared to HER, due to its relatively sluggish kinetics and high overpotential [6,7].

Therefore, significant emphasis has been directed towards conducting research to identify cost-effective, active, and stable electrocatalysts for promoting OER.

Over the past decades, efficient OER catalysts have been mainly based on precious metals and their oxides such as IrO_2 and RuO_2 . Due to their high costs, alternative materials such as transition metal oxides have been explored as electrocatalysts for OER. For example, Shao-Horn's group has shown that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ has much better catalytic activity than the state-of-the-art IrO_2 [8]. They also pointed out that the highest OER activity could be achieved when the electron occupancy of the metal e_g orbital is close to unity [8]. Based on the e_g orbit theory, Xu's group tailored the Co-O bonding covalency via substituting Fe with Co in LaCoO_3 [7]. They found that $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ exhibits the

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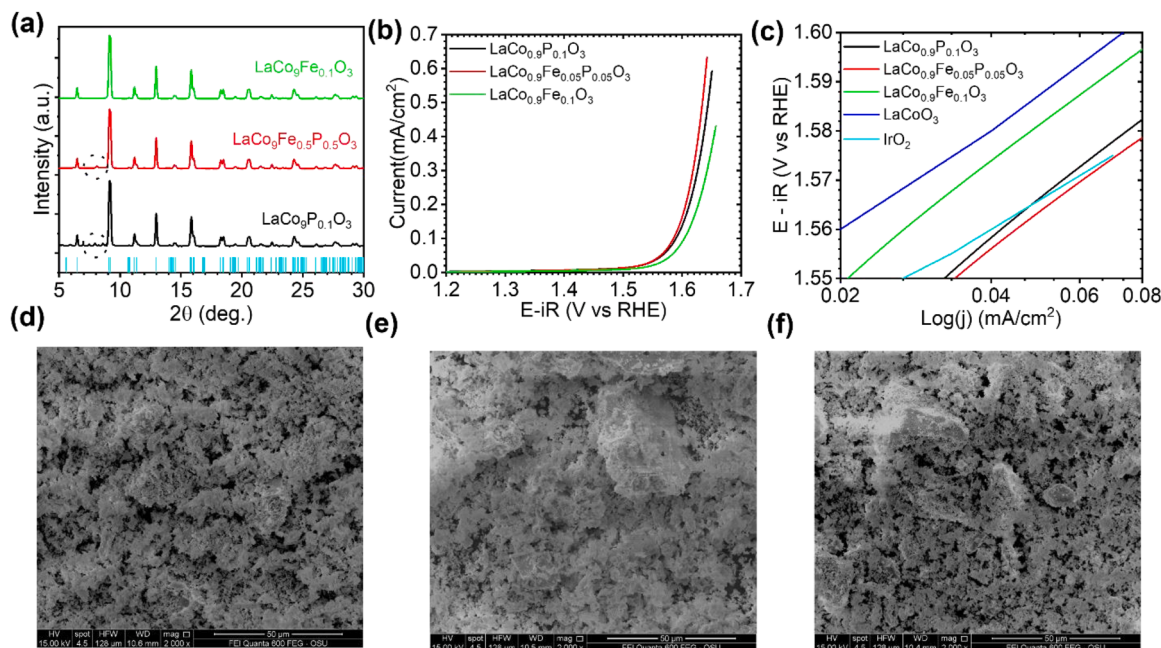


Fig. 1. (a) XRD diffraction with LaCoO_3 standard at bottom (b) OER performance of $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$, $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$, and $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ (c) Tafel plot of different peroxides compared with unsubstituted LaCoO_3 extracted from Ref 7 and benchmarked IrO_2 extracted from Ref 11; SEM of (d) $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$, (e) $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$, and (f) $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

best OER performance among different percentages of Fe substitution due to the highest transition-metal-oxygen-bonding covalency (TMOBC) [6]. Recently, the P substitution has been explored as an alternative approach to enhance the OER performance of perovskites [9,10]. For example, Chen's group found that the high-valence-state P substitution in $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ enhances the OER performance, which is attributed to the introduction of more oxygen vacancies. Different from metal substitution, P substitution in perovskite oxides provides a non-metallic site. This challenges the metal-centered theory (e.g., e_g orbital theory) and requires more fundamental understanding of the influence of anion substitution, or more generally the role of cation and anion substitution

in perovskite oxides electrocatalysts.

In this work, we substituted Fe and P into LaCoO_3 to understand the role of cation and anion doping such as whether P could adjust TMOBC similar to Fe. This is the extension of the previous work on Fe doping in LaCoO_3 [7]. The electrochemical performance indicates the P doping could improve the OER catalytic performance, and Tafel slope suggested that P doping does not change the reaction mechanism. With the help of multimodal characterization tools including *operando* X-ray diffraction (XRD) and *operando* hard X-ray absorption spectroscopy (XAS) together with electrochemical performance, we revealed that those materials, particularly the metal sites, did not undergo any obvious crystal and

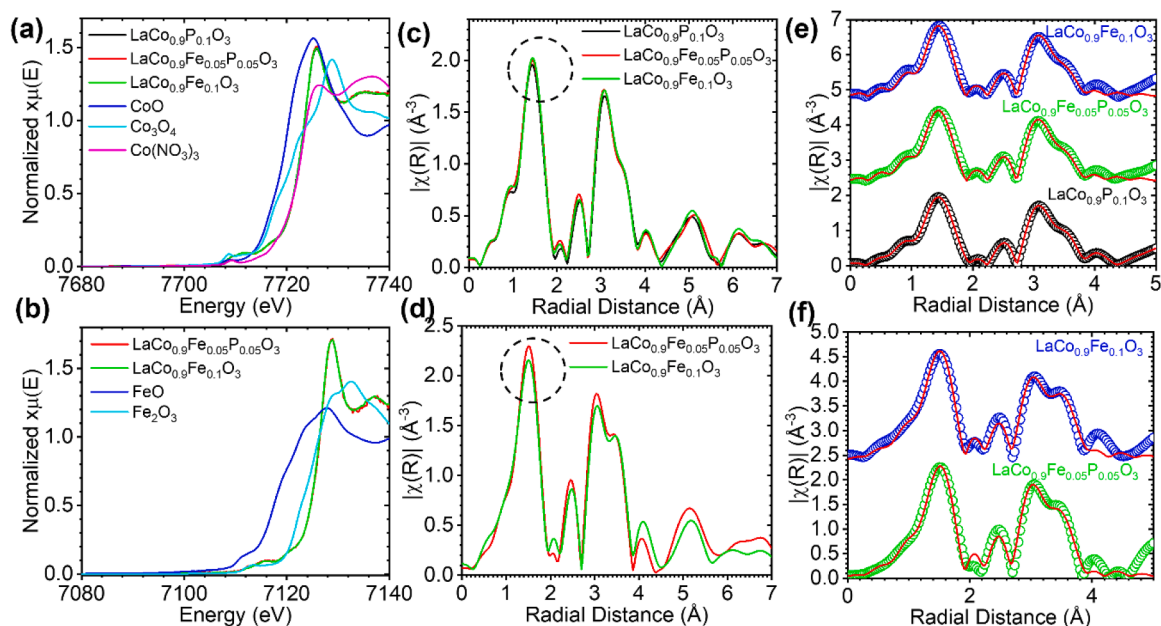


Fig. 2. Co K-edge (a) XANES (c) Fourier Transform R-space (e) R-space fitting (the dot are the raw data and solid line are the fitting data); Fe K-edge (b) XANES (d) Fourier Transform R-space (f) R-space fitting (the dot are the raw data and solid line are the fitting data) of $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$, $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$, and $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

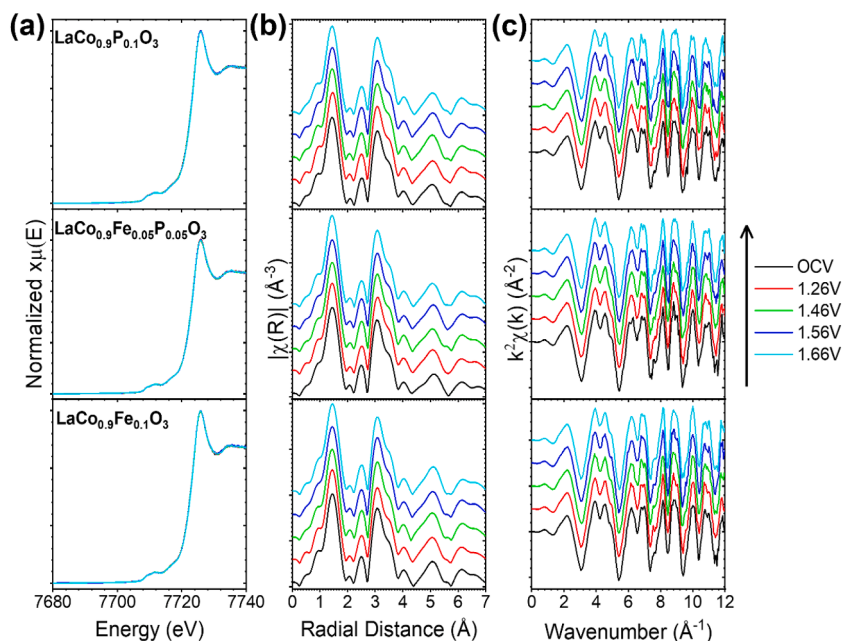


Fig. 3. Operando Co K-edge (a) XANES (b) Fourier Transform EXAFS in R-space (c) and EXAFS in k-space for $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$, $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$, and $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

local structure changes under OER conditions, which suggests that the cation may not be the only reaction center. Furthermore, *ex-situ* soft XAS illustrated that P substitution did not change neither Co nor Fe electronic structure or crystal structure but did change TMOBC. Therefore, by combining O K-edge XAS with the density functional theory (DFT) analysis, we provided a new way to explain the enhanced OER performance: the hybridization between e_g orbitals and O 2p orbitals is more critical to determine the OER performance in oxide electrocatalysts.

2. Results and discussion

XRD was carried out to reveal the crystal structure of $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$, $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$, and $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ (Fig. 1a). All three materials show the rhombohedral structure, which is the same as pure LaCoO_3 and there is no phase transition change caused by Fe and P substitution. Rietveld refinement was carried out to further confirm the lattice parameter change (Fig. S1 & Table S1). There are some small lattice changes of the three materials which may be caused by the Fe and P doping. In addition, some low-angle peaks were missing in $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$ and $\text{LaCo}_{0.95}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$ from the refinement when using the LaCoO_3 crystal structure. This indicates the P doping of B-site as suggested in the previous study [9–11]. To quantify the surface area of $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$, the Brunauer-Emmett-Teller (BET) tests were carried out and the specific surface areas of these $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ were measured to be around $3.6 \text{ m}^2/\text{g}$ (Table S2). Scanning electron microscopy (Fig. 1d–f) confirms that all those materials have similar morphology. Energy dispersive spectroscopy (EDS) was also carried out to ensure that we successfully substituted Fe and P into the LaCoO_3 (Fig. S2). The element distribution ratio estimated from EDS (Table S3) confirms the expected composition of the synthesized materials. By carefully estimating the atomic ratio of Fe, Co, and P with La, it suggests that $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$ has around half amount of P compared with $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$ and half the amount of Fe compared with $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$. This also confirms the P and Fe doping in B-site [11]. The OER performance of $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ was tested in 0.1 M KOH solutions using the three-electrode rotating disk method. The OER current normalized with the BET surface area indicates that $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$ has the best OER performance (Fig. 1b) with the lowest onset potential (i.e., 1.60 V at $0.2 \text{ mA}/\text{cm}^2$), and the $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ shows the worst OER performance (i.e., 1.63 V at $0.2 \text{ mA}/\text{cm}^2$). Note that our $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$

exhibits the same OER performance as described in previous literature (i.e., 1.63 V at $0.2 \text{ mA}/\text{cm}^2$) [7], which confirms that our P-substitution further enhances the OER catalytic activity, but still little worse than standard RuO_2 (Fig. S3). The better OER activity of Fe and P doped oxides in our study is also reflected by the comparison of Tafel slopes of our samples with those reported in literature, including IrO_2 (Fig. 1c) [7, 12]. However, the slope of Tafel plots are very close around four materials, which indicates the similar reaction mechanism or reaction pathway. Hence, the difference between catalytic performance is more likely related to materials' intrinsic characteristic parameters.

Ex-situ XAS was carried out to obtain the valence state, electronic structure, and local structure of both Co and Fe (Fig. 2a&b) [13–16]. Although the shapes of X-ray absorption near edge structure (XANES) spectra of our electrocatalysts are different from $\text{Co}(\text{NO}_3)_3$ and Fe_2O_3 due to different local structures of perovskites and standards (Fig. 2a&b), all three $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ show the same Co and Fe valence states with Co valence state close to Co(III) and Fe with slightly higher valence state than Fe(III) [7,13], which suggests that the substitution does not change the oxidation state to influence the OER performance. Note that a minor spectra difference (highlighted by circles in Fig. 2e&f) on extended X-ray absorption fine structure (EXAFS) of Fe and Co may be caused by the Fourier transformation of the noise in the k-space (Fig. S4) or the actual oxygen vacancy. Since the oxygen vacancy would also plays a critical role in the OER catalytic performance, we carried the model based (LaCoO_3 as the study model) EXAFS fitting to estimate the oxygen coordination with both Co and Fe (Fig. 2e, f & S5). Based on the EXAFS fitting results (Table S4&5), there is only tiny Co-O/Fe-O coordination number difference three samples. Considering the error bar, those slight differences may be caused by the noise point in the k-space or some small amount of oxygen vacancies formation on the surface due to P doping. However, the amount of oxygen vacancies are not significant, which do not play a critical role in the OER performance. Hence, the P substitution does not induce different OER performance through alteration of the metal oxidation state or local structure.

To further understand the OER reaction mechanism and how P-substitution is achieved, the *operando* characterizations under catalytic reaction were carried out. *Operando* XRD (Fig. S6) showed no change in the bulk crystal structure for all three materials, which confirms that the OER only takes place on the surface of the materials. *Operando* XAS

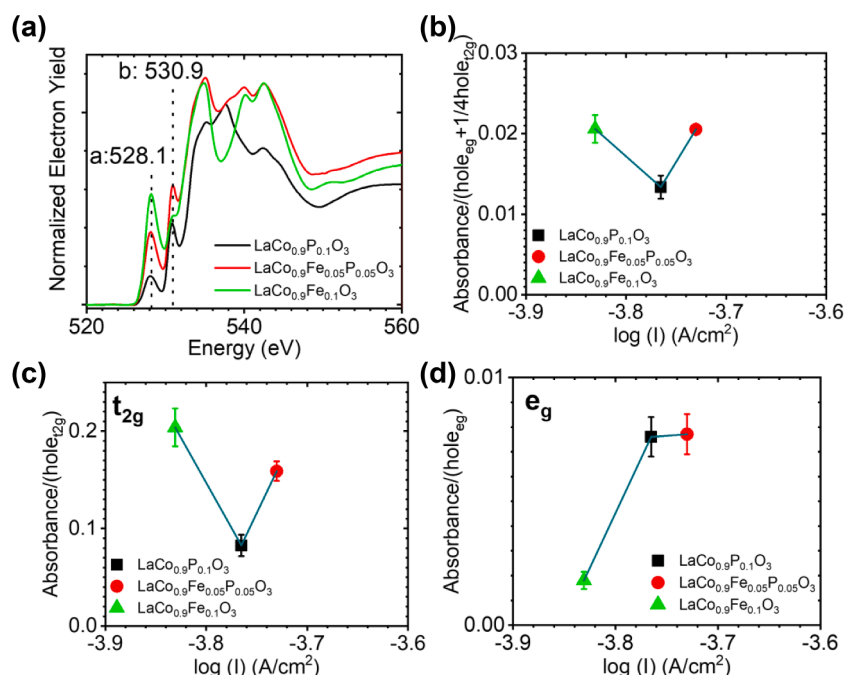


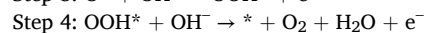
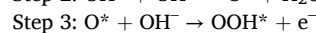
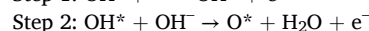
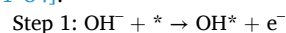
Fig. 4. (a) O K-edge XAS, (b) estimated TMOBC based on the total area of peaks a and b, (c) estimated transition metal t_{2g} and O 2p hybridization based on the area of peak a, (d) estimated transition metal e_g and O 2p hybridization based on the area of peak b for $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$, $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$, and $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ (The current density for comparing is the current at overpotential equaling to 0.3 V).

measurements were also carried out to probe any electronic structure or local structure change during the OER (Fig. 3&S7) [17,18]. Based on the Co K-edge XANES, there is no Co electronic structure change in the $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ materials during the catalytic reaction (Fig. 3a). In addition, no change in Co local structure of the $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ materials was observed (Fig. 3b&c). The *operando* Fe K-edge XAS measurements (Fig. S7) provide similar results. These results showed no electronic or local structure changes in the materials during the catalytic reaction. Note that XAS is a bulk-sensitive technique. Since most of the bulk Co and Fe are not involved in the reaction, changes in the surface Co and Fe could be below the XAS detection limit [19]. In addition, a previous study used a surface-sensitive hard XAS to indicate only a small amount of LaCoO_3 on the surface undergoes catalytic reaction [20]. It is also possible that the bulk oxygen is involved in the catalytic reaction, which may not cause any structure change of Co and Fe [21]. Therefore, the surface sensitive *ex-situ* soft XAS at Fe L-edge and Co L-edge were also carried out to probe the surface Fe oxidation state and the electronic structure using electron yield mode [16]. Although there is slightly difference in L3 peak of both Co and Fe for all electrocatalysts, but the peak location and distribution are the same around three materials, (Fig. S8), which indicates the almost same surface oxidation state (Co(III) and Fe(III)) and electronic structure [22–27].

As no electronic structure and local structure changes were identified at the cation site, the e_g orbital theory based on 3d transition metal does not work well to explain the increased OER performance of the $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ materials. Therefore, the TMOBC theory, another important descriptor for perovskite OER performance [7,8], was considered to explain the electrocatalytic performance. Surface-sensitive O K-edge XAS measurements were carried out to estimate the TMOBC (Fig. 4a) [27–30]. The P substitution has a significant influence on the O K-edge spectrum. Fig. 4a shows peak a and peak b can be used to estimate the TMOBC. Their changes emphasize the difference in metal-oxygen covalency of the three $\text{LaCo}_{0.9}\text{Fe}_x\text{P}_{0.1-x}\text{O}_3$ materials, which could explain the different OER catalytic activities. The areas of peak a and peak b were further analyzed to quantify the strength of TMOBC. Based on the method mentioned in previous literature [22,30] and our soft XAS study [27], Co and Fe were treated as Co(III) with

intermediate spin and Fe(III) with high spin, respectively, based on the Co and Fe L-edge soft XAS data (Fig. S8) and their similarities in spectra shapes reported in literature [7,8,22,24,26,27]. The results (Fig. 4b) illustrate that $\text{LaCo}_{0.9}\text{Fe}_{0.05}\text{P}_{0.05}\text{O}_3$ has the strongest TMOBC, which can be correlated to the best OER performance among the three materials and is consistent with previous reported trend [7,22]. However, the $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ that exhibited worse OER performance than $\text{LaCo}_{0.9}\text{P}_{0.1}\text{O}_3$ showed stronger TMOBC strength. This opposite trend suggests that more detailed analysis or alternative theory is needed. When transition metal cations are involved in adsorption, desorption and formation of a surface chemical bonds of the reaction intermediates, the materials' chemical properties are mainly determined by the outermost antibonding orbital 3d e_g while 3d t_{2g} is less involved. Thus, the hybridization of the transition metal 3d e_g and the oxygen 2p is more influential in electrocatalysts' activity than that of the transition metal 3d t_{2g} and the oxygen 2p. For O K-edge XAS spectrum, peak a reflects the transition metal t_{2g} and O 2p hybridization and peak b can be treated as the transition metal e_g and O 2p hybridization [28]. Their estimated hybridizations are shown in Fig. 4c and d, respectively. Clearly, the trend of TMOBC strength shown in Fig. 4d matches that of the OER activity of the three electrocatalysts, suggesting that the hybridization between metal e_g and oxygen 2p is the dominate factor. Comparatively, the TMOBC strength in Fig. 4c, which reflects the metal t_{2g} and O 2p hybridization, fails to explain the three electrocatalysts' OER activity. Hence, we propose a new descriptor for perovskite OER catalytic performance: the greater transition metal e_g orbital hybridization with O 2p orbital leads to higher OER performance.

In alkaline media, the widely accepted OER mechanism on metal oxides consists of the following four-electron/proton transfer steps [31–34]:



The first step describes a hydroxyl radical adsorbed on the active site (*) to give OH^* by 1 e^- oxidation of hydroxide anion (OH^-). Then the coupled proton and electron removal from OH^* leads to O^* in the second

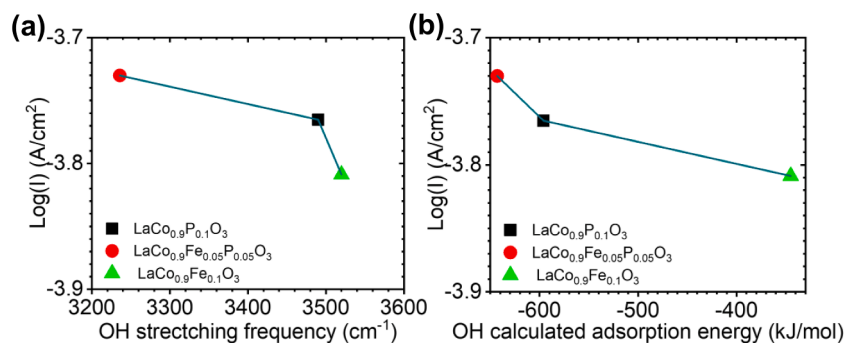


Fig. 5. (a) Plot of the log of the experimental current density (at 0.3 V overpotential) vs DFT stretching frequency of OH on different Perovskite structure (b) Plot of the log of the experimental current density (at 0.3 V overpotential) vs DFT adsorption energy of OH on different Perovskite structure.

Table 1

ICOHP and ICOBI of Co-O atom pair close to the dopant atom.

Surface dopant	ICOHP Pristine	Fe/P	Fe	P	ICOBI Pristine	Fe/P	Fe	P
Atom pair	Co-O	Co-O	Co-O	Co-O	Co-O	Co-O	Co-O	Co-O
Spin-up	-0.927	-0.915	-1.012	-0.388	0.146	0.143	0.168	0.036
Spin-down	-1.040	-1.042	-1.026	-0.589	0.149	0.150	0.156	0.060

step. Furthermore, coupled with 1 e⁻, O* is attacked by hydroxyl anion to form the hydroperoxide intermediate OOH* in the third step and a further proton-coupled electron transfer in the fourth step releases O₂ and regenerates the free active site. Clearly, the adsorption and interaction of OH group is critical to facilitate the oxygen evolution. Researchers have suggested that the OER activity of oxides is correlated with the metal–OH bond strength [35,36], which supports our conclusion that metal-oxide covalency, particularly, transition metal e_g orbital hybridization with O 2p orbitals, can be the property descriptor for oxides' OER activity. To further confirm this correlation, DFT calculations were carried out to estimate the surface interactions of OH groups on different surfaces (Fig. 5 & Table S6). Previous studies have shown a linear relationship between the adsorption energy of OH and OER performance of Perovskites [36–38]. Similarly, we observed that the experimental OER performance increases with decrease in the calculated adsorption energy of OH on the perovskite and OH stretching frequency (see Fig. 5a). The lowest adsorption energy of OH is on the LaCo_{0.92}Fe_{0.04}P_{0.04}O₃ perovskite. The lower adsorption energy enhances the first elementary reaction step (OH⁻ + * → OH* + e⁻) of OER. Fig. 5b shows how the OER activity increases with lower OH stretching frequency (longer adsorbed OH bond length) and weaker OH bond making the second elementary reaction step (OH* + OH⁻ → O* + H₂O + e⁻) of the OER easier to occur. This second elementary step involves shuttling of a hydrogen from the surface species to OH⁻, forming H₂O in the solution and the weaker OH bond enhances that shuttling of H into the solution. The DFT results confirm the experimental trend that LaCo_{0.9}Fe_{0.05}P_{0.05}O₃ has the best OER performance with the lowest overpotential, and the LaCo_{0.9}Fe_{0.1}O₃ shows the worst OER performance. This supports our claim that metal-oxygen hybridization between transition metal e_g orbitals and O 2p orbitals could be a good activity descriptor for OER.

The projected Crystal orbital Hamilton population (COHP) for the Co-O atom pair close to the dopant atom in the different surfaces is shown in the SI. (Fig. S13) [39,40] The integrated COHP (ICOHP) and Integrated crystal orbital bond index (ICOBI) are shown in Table 1. The ICOHP and ICOBI calculations indicate an increase in Co and O coupling with Fe doping while it remains similar with Fe and P co-dopants. However, the coupling strength decreased when doped with P only. This is in quantitative agreement with the TMOBC in Fig. 4b and c where Fe doped perovskite has the strongest metal-O bond strength, followed by Fe/P and P doped. (Table 1) ICOHP for La, Co, Fe, and P-O (H) atom

pair on the different surfaces are shown in the SI. (Table S7)

3. Conclusions

In summary, we have studied the role of metallic (Fe, Co) and nonmetallic (P) substitution to tune the OER catalytic performance of perovskites. We observed an increased OER catalytic activity with co-substitution of P and Fe due to the change in TMOBC. Although no changes in catalyst structure and cation redox were observed, differences in metal-oxygen covalency were identified for these catalysts, which is the critical factor resulting in the different OER activities. Based on detailed surface-sensitive O K-edge XAS analysis, we propose that the greater transition metal e_g orbital hybridization with O 2p orbitals leads to higher OER performance, which combines the e_g orbital theory and TMOBC theory in one new descriptor. Such correlation was confirmed by DFT calculation on the adsorption energy of OH on the perovskite and OH stretching frequency. This study provides deep insights into the effect of electronic structures on the OER kinetics and mechanisms, as well as guidance for the development of more active oxide catalysts for OER in the future.

Author contributions

M.W., and Z.F. conceived the project. M.W. and B. M. synthesized the materials and carried out the electrochemical measurements. K.C. carried performed DFT calculations. S.K. performed the COHP and COBI analysis. W. S carried out the *in-situ* XRD measurements. Z. H. and L.F. did the BET measurements. M. L. did the EDX and SEM measurements. M.W., C.C., A.C., and A.D. performed *ex-situ* soft XAS measurements and analysis. M.W., G.S., and Z.F. carried out the *in-situ* and operando XAS measurements and analysis. M.W., K.C., L.A., and Z. F. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2023.143034](https://doi.org/10.1016/j.electacta.2023.143034).

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