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Enlarged Co-O covalency in octahedral sites leading to highly efficient spinel oxides for oxygen evolution reaction

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Co-containing spinel oxides are promising electrocatalysts for oxygen evolution reaction (OER) owing to its remarkable activity and durability. However, its activity still needs further improvement and related fundamentals remain untouched. The fact that spinel oxides tend to form cation deficiency could differentiate their electrocatalysis from other oxide materials, e.g. the most studied oxygen-deficient perovskites. Here, a systematic study of spinel $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides ($x=0\sim 2.0$) toward OER is presented and a highly active catalyst superior to benchmark IrO_2 is developed. The distinctive OER activity is found to be dominated by the metal-oxygen covalency and an enlarged Co-O covalency by 10 ~ 30 at% Fe substitution is responsible for the activity enhancement. While the pH-dependent OER activity of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ (the optimal one) indicates decoupled proton-electron transfers during OER, the involvement of lattice oxygen is not considered as a favorable route because of the downshifted O p-band center relative to Fermi level governed by the spinel's cation deficient nature.

The escalating demands for energy resources across the world are speeding up the depletion of fossil fuels and have generated severe environmental issues. Gradually replacing the fossil energy infrastructure with a clean and sustainable one is an important aspect that human being should put considerable effort into. Hydrogen gas, which can be harnessed from the water electrolysis, is believed as an ideal energy carrier in the future clean energy infrastructure. However, the energy efficiency of the water electrolysis is hindered by the high overpotential of the oxygen evolution reaction (OER) at the anode. To date, IrO₂ and RuO₂ have been identified as the benchmark catalysts for OER. However, the scarcity and high price of Ir and Ru have cast shadow over its wide application. Thus, considerable effort is now being given globally in searching low-cost OER catalysts as alternatives.^[1] Transition metal spinel oxides appear to be a class of promising candidates owing to their element abundance and remarkable activities. Special attention has been given to some Co-containing spinel oxides as they afford high catalytic OER activity and durability.^[2] Substituting Co with other transition metals (TMs) in spinel has been found influential on tuning their catalytic activities. For example, substituting some Co with Zn (e.g. Zn_xCo_{3-x}O₄^[2d]) or Ni (e.g. Ni_xCo_{3-x}O₄^[3]) in Co₃O₄ may promote the OER over the pure Co₃O₄. The activity enhancement is preliminarily explained by the substitution induced morphology change.^[2d, 3] The more insightful explanation about the intrinsic origins remained untouched. This contrasts starkly with the impressive progress made towards the fundamental understanding of OER on perovskite oxides.^[4] The interaction between B-site TM 3d and O 2p states has been the major perspective that have guided the exploration of distinctive OER origin.^[4a, 4d, 5] As TM e_g orbital exhibits a strong spatial overlap with O 2p orbital, the e_g occupancy, co-determined by the d electron number and spin state, has been concluded as the catalytically-critical factor.^[4a] The correlations made between OER activity and e_g states were

built under a four-step concerted proton-electron transfer mechanism.^[4a] Most recently, the new understanding on the lattice oxygen participated OER has been revealed on some perovskite oxides^[6] and increased metal-oxygen covalency has been considered critical in promoting the OER kinetics.^[6b, 7]

It is expected that these insightful findings can bring inspirations to the understanding of OER by spinel oxides because spinel structure contains octahedra TMO_6 unit as that of perovskite oxides.^[8] Challenges still exist because, on one hand, the defect chemistry perspective suggests apparent catalytic differences between the two crystal families. It is noteworthy that the state-of-the-art perovskite OER catalysts (mostly Co-based perovskite oxides, e.g. BSCF_{82} ,^[4a, 9] $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$,^[6b] $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$,^[10] and etc.^[11]) generally possess oxygen-deficient compositions. The concentration of oxygen vacancies on the surface was claimed to be orders of magnitude higher than that in the bulk.^[12] It means the oxygen-deficient nature could greatly modify the surface reactions. The surface oxygen deficiencies in perovskite has been proposed to be a critical component in triggering or facilitating the oxygen-exchange mechanism.^[6a, 10] In contrast, most of the spinel oxides tend to have cation deficiencies (an oxygen-excess nonstoichiometry)^[8a, 13] and exhibit p-type conductivity. This could actually make a difference to the mechanistic understanding of OER by spinel materials. On the other hand, the fact that spinel also contains tetrahedral geometry makes the catalytic reactions more complicated. As TMs have different geometric preferences, it generally produces structure reversal in mixed-spinel oxides. The structure reversal has been reported to be an influential factor on electrocatalysis.^[14] The key in interpreting the OER by the structure reversal depends greatly on the modified octahedral environment.^[8a, 14b]

To deepen the understanding of OER on substituted spinel oxide, a series of $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$

oxides ($x=0\sim 2.0$) were examined as OER catalysts. The incorporation of Zn aims to fix the spinel to a normal structure and gain exclusive information on the catalytically-critical octahedra. In addition, it helps create a cation-deficient surface that differs from the Co-perovskites because Zn spinels are generally categorized as p-type conducting oxides.^[13] Utilizing X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculation, a correlation between the OER catalysis and Co-O covalency has been established. Non-concerted proton-electron transfers has been considered possible in spinel oxides as the best-performing $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ catalyst displays significant pH dependence in OER. However, unlike the lattice oxygen-mediated OER mechanism revealed in perovskites,^[6b, 7] we highlight the differences in the decoupled proton-electron transfer pathways of spinel oxides owing to its cation-deficient nature.

The crystal structures of the synthesized $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides ($x=0\sim 2.0$) were confirmed by X-ray diffraction analysis (XRD). As shown in **Figure 1a**, the diffraction peaks of the as-synthesized ZnCo_2O_4 and ZnFe_2O_4 fit well with that of the standard spinel oxides. Only a gradual peak shift to lower angles can be observed as the Fe content increases in $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides. The peak shifts, indicating certain changes in the lattice parameter, are mainly due to the differences in ionic radius of Fe and Co elements. X-ray absorption fine structure (XAFS) technique was performed to probe the valence state and local structure of TM in $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides. The X-ray absorption near edge spectroscopy (XANES) shows that the absorption edges of Zn overlap well with that of ZnO (Figure 1b). It signifies that the Zn cations are of a valence state of +2 (Figure 1e). While the edge energies of Fe almost remain unchanged (Figure 1c), the absorption edges of Co exhibit significance shifts (Figure 1d). The quantified valence states by an integral method^[15] (Figure 1e) show that valence state of Fe remains at

around +3 and that of Co ranges from $\sim +2.86$ to $+3.34$. The chemical formulas of the various spinel oxides can be approximated as $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_{4+\delta}$, where δ indicates the oxygen non-stoichiometry and ranges from ~ 0 to 0.27 .^[8a, 16] The Fourier transform (FT) extended X-ray absorption fine structure (EXAFS) spectra (Figure S1 and S2) shows two interatomic metal-metal distances at $\sim 2.5 \text{ \AA}$ ($\text{TM}_{\text{Oct}}\text{-TM}_{\text{Oct}}$) and $\sim 3 \text{ \AA}$ ($\text{TM}_{\text{Td}}\text{-TM}_{\text{Td}}/\text{TM}_{\text{Td}}\text{-TM}_{\text{Oct}}$) for Co/Fe K-edge and one metal-metal distance at $\sim 3 \text{ \AA}$ for Zn K-edge. This indicates that Zn cations only occupy the tetrahedral sites.^[8b] The near normal spinel structure was further confirmed by the EXAFS curve fitting (Figure S1c and Table S1). The exclusive occupation of Fe and Co in octahedral sites indicates that the catalytic contribution of the investigated spinel oxides should be mainly from the edge-sharing $\left[\text{Fe}_{\frac{x}{2}} \text{Co}_{1-\frac{x}{2}} \text{O}_6 \right]$ octahedra unit.

As some of the spinel oxides are of oxygen-excess non-stoichiometry, we examined the formation energy of point defects (i.e. oxygen interstitial (O_i) and Zn vacancy (Zn_v)) in the spinel lattice. The calculated defect formation enthalpies are summarized in **Table 1** (DFT methodology can be found in the Supporting Information). The formation enthalpies of Zn_v are less than that of O_i in each model spinel crystals (ZnCo_2O_4 , and $\text{Fe-ZnCo}_2\text{O}_4$), which indicates that the formation of Zn_v is more thermodynamically favorable than that of O_i . In addition, the lower Zn_v formation enthalpies in the substituted spinels than in ZnCo_2O_4 suggests that the incorporation of Fe has promoted defects formation in the spinel lattice. The existence of Zn vacancies was detected in the most non-stoichiometric compositions as the ICP-OES (Inductively coupled plasma-optical emission spectrometry) results show that the atomic ratio of $\text{Zn}:(\text{Co}+\text{Fe})$ is ~ 0.44 to 0.47 (Table S2). To further examine the TM electronic structure changes induced by the substitution in the spinel lattice, Bader charge analysis was conducted. Crystal models of ZnCo_2O_4 and $\text{Zn}_v\text{-Fe-ZnCo}_2\text{O}_4$ (Figure S3) were built in order to achieve

theoretical and experimental consistency. To be specific, we introduced Zn vacancies in the substituted spinel models, but not ZnCo_2O_4 . This is because our XANES results show that the substituted spinels (with relatively lower Fe concentration) are further from stoichiometric than that of ZnCo_2O_4 . In addition, the defect calculations demonstrate that the generation of Zn_V in $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ is more thermodynamically favorable than that in ZnCo_2O_4 . As shown in Table S3, the average charge of Co atoms in perfect ZnCo_2O_4 structure is 7.6532. With replacing one of the 16 octahedral Co atoms with Fe, the average charge of Co drops to 7.6517 in $\text{Zn}_\text{V}\text{-Fe-ZnCo}_2\text{O}_4$. The Bader charge and magnetic moment of Fe in $\text{Zn}_\text{V}\text{-Fe-ZnCo}_2\text{O}_4$ are 6.27 and 3.97 μB , respectively, signifying the very existence of Fe^{3+} .^[17] It suggests that the electron hopping between Fe and Co is quite unlikely because Fe^{3+} can hardly be oxidized.^[18] Alternatively, there is greater tendency for electron-deficient Zn vacancies to withdraw electron density away from Co, resulting in the increase of Co valence state. Thus the observed Co valence states (slightly higher than +3) in some $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides ($x=0.2, 0.4$ and 0.6) is not surprising. From the DFT analysis, the alteration of Co electronic state by Fe substitutions has been illuminated and is consistent with the XANES result.

The spinel $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides were then tested for their electrocatalytic OER performance (Figure S4). **Figure 2a** shows the representative OER CV curve of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ recorded within a potential window of 1.0~1.7 V (vs. RHE) in O_2 -saturated 0.1 M KOH and the positive-going OER curves after background and iR-correction.^[8a, 19] As catalytic OER only involves the surface atoms, catalytic activity based on catalysts' surface area, instead of electrode geometric area, reflects the intrinsic activity of a given catalyst.^[20] Thus, the background- and iR-corrected OER kinetic currents are normalized by the surface area of oxides to extract the specific activity shown in Figure 2b. The surface areas of spinel oxides were determined by

BET measurements (shown in Figure S5 and Table S4), as extracting the specific activity of powder catalysts by BET surface area is a well-established methodology.^[4a] As shown in Figure 2b, the OER activities of $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2$) oxides span across a potential window of ~ 130 mV and the activity difference between ZnCo_2O_4 and ZnFe_2O_4 is ~ 2 orders of magnitude. Consider ZnCo_2O_4 as benchmark here, Fe substitution may either cause a promotion on the OER or a demotion, depending on the substitution amount. Potentials required to drive a current density of $25 \mu\text{A cm}^{-2}_{\text{ox}}$ are mapped out in Figure 2c. The OER activity is promoted by a relatively small amount of Fe substitution ($x=0.2\sim 0.6$), as indicated by the reduced overpotentials (of ~ 35 mV in maximum) compared with that of ZnCo_2O_4 . On the contrary, activity deteriorations are detected with high Fe substitution amounts ($x=1.0\sim 2.0$). The OER of commercial IrO_2 was tested following a consistent procedure described for the $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ catalysts (details can be found in Supporting Information). The linear sweep voltammetry (LSV) of the IrO_2 is compared with that of the best-performing $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ in the inset of Figure 2d. It clearly suggests that the $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ is a promising candidate for replacing commercial IrO_2 . The stability test (over 5000 cycles) run for the $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ oxide (Figure 2d, Figure S6) demonstrate that the durability requirements are also met. The slight increase of current could be due to the leaching of Zn (small amount) and a largely hydroxylated surface (Figure S7).^[21] It is worth mentioning that the carbon additive (AB) (e.g. carbon corrosion) is not likely to be responsible for such current change because the background current from carbon is rather negligible (Figure S8).

A fundamental understanding on the substitution effects is of paramount importance for screening and designing highly efficient Co-containing spinel oxide catalysts for OER. The transmission electron microscope (TEM) images (Figure S9) show that the various $\text{ZnFe}_x\text{Co}_{2-x}$

$x\text{O}_4$ oxides are made up of irregularly shaped particles. The random stacking of these irregularly shaped particles produced uniform microscale (~ 25 nm) pore structures observed in the scanning electron microscope (SEM) (Figure S10) and BET results (Figure S11). The morphology is therefore not considered as an influencing factor for the distinctive OER performance of $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides. The start-up step of one single OER cycle in alkaline electrolyte involves the adsorption of OH^* . That is the hybridization between TM 3d orbitals and O 2p orbitals of OH^* . The Fe substituents, which present as Fe^{3+} ($t_{2g}^3 e_g^2$) in the various $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides, bind the oxygen too weakly and fail to activate the reactant.^[4a] We, therefore, assume that the Co are the major active sites in those Co-containing spinel $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides. As the majority of Co possesses a valence state of $\sim +3$ or a mixture of $+3/+4$, the molecular orbital diagrams of $\text{Co}^{3+}\text{-OH}$ and $\text{Co}^{4+}\text{-OH}$ on the spinel oxide' surface are shown in **Figure 3a**. Compared with Co^{3+} , Co^{4+} has a low energy 3d states and would produce higher hybridization due to the shortened energy distance between the TM 3d and O 2p states.^[22] It is reported that the metal-oxygen covalency factor (i.e. charge transfer energy) bridges the understanding of OER via different reaction mechanisms.^[4d] Thus, we discuss the OER activity of the investigated spinel oxides as a function of Co-O covalency in Figure 3b. With the OER activity displayed by the potentials required to drive a specific current density of $25 \mu\text{A cm}^{-2}_{\text{ox}}$, the Co-O covalency is predicted by the parameter $N-V$ (N is the number of unpaired electrons of Co atom, V is the nominal valence state of Co cation.).^[6a] The lower the $N-V$ value, the greater the TM-O covalency.^[6a] This is because the parameter $N-V$ is indicative of the net ability of TM cation to donate electrons. The lower the ability of the TM to donate electrons to the oxygen, the higher the probability that the TM drags the electronic density slightly away from the oxygen atom and thus leading to a greater TM-O covalency.^[6a] As displayed in Figure 3b, the

parameter N-V well describes the OER activity of the substituted spinel oxides. To be specific, an increased Co-O covalency gives a higher OER activity and vice versa.

To further confirm this hypothesis, electronic density of states (DOS) calculations for ZnCo_2O_4 and $\text{V}_{\text{Zn}}\text{-Fe-ZnCo}_2\text{O}_4$ were conducted to give more accurate determination (Figure S12). Figure 3c and 3d show the calculated PDOS and crystal models for bulk ZnCo_2O_4 and $\text{V}_{\text{Zn}}\text{-Fe-ZnCo}_2\text{O}_4$. Specifically, the valence band (spreads over ~ 8 eV range) and the lowest conduction band are displayed. As shrinking energy difference between the TM 3d and O 2p-band centers indicates an increased metal-oxygen covalency,^[4d] the Co 3d and O 2p centers are determined for ZnCo_2O_4 and $\text{V}_{\text{Zn}}\text{-Fe-ZnCo}_2\text{O}_4$ by integrating the PDOS. Our results (Table S5) show that compared with ZnCo_2O_4 , the Co 3d and O 2p centers get closer in $\text{V}_{\text{Zn}}\text{-Fe-ZnCo}_2\text{O}_4$, suggesting that the $\text{V}_{\text{Zn}}\text{-Fe-ZnCo}_2\text{O}_4$ oxide exhibits greater Co-O covalency than ZnCo_2O_4 . The enlarged Co-O covalency can promote the electron transfer between the TM cation and oxygen adsorbates (e.g. O_2^{2-} , O^{2-}) or facilitate the injection/extraction of electrons from oxygen, thereby accelerating the OER rate.^[4c, 22b]

In addition to the influencing role of Co-O covalency on the OER activity, the metal-oxygen covalency was also proposed to be a governor of the reaction mechanism.^[4d, 6] With increasing metal-oxygen covalency, the OER tends to transfer from a concerted proton-electron transfer pathway to a decoupled proton-electron transfer.^[4d, 6a] The OER performance of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ was then examined in KOH electrolyte with different pH. The background and iR-corrected OER curves are shown in **Figure 4a**. It is apparent that the catalytic activity exhibits strong pH dependence. Within the investigate pH range, an electrolyte (KOH) concentration of 1 M produces the highest OER activity. This emphasizes the need for one to search for the optimal catalyst at the optimal pH. As displayed in Figure 4b, the overpotential and Tafel slope of

$\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ at pH 14 are compared with that of Co-based oxides and state-of-the-art IrO_2 and RuO_2 (Figure S13).^[5b, 8a, 23] The comparisons made suggest that the developed spinel $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ is a highly efficient OER electrocatalyst. It is known that the pH dependence indicates the existence of non-concerted proton-electron transfer in catalytic reactions.^[24] To better illustrate this, alternative decoupled proton-electron transfer pathways of an exemplary rate-limiting OER step (Figure S14)^[4a, 8a] are displayed in Figure 4d. Specifically, the conventional concerted proton-electron transfer occurs along the diagonal and the two alternative decoupled pathways are shown along the edges of the square scheme. According to recent findings, one of the potential pathways of non-concerted proton-electron transfer during OER could involve the redox of lattice oxygen.^[6b] The lattice oxygen being the active sites is generally featured with a decreased OER stability over cycling (especially for the first 50 cycles at a scan rate of 10 mV s^{-1}).^[6a] Interestingly, the activity enhancement of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ oxide over the first 50 cycles (Figure S6a, 6b) is much less significant in comparison with the well-identified oxygen active-perovskite catalysts.^[9] Catalyst $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ shows only ~ 1.2 times greater current than its initial one over 50 cycles while the oxygen active-perovskite, e.g. BSCF82,^[9] exhibits ~ 4 times current increase. Under the lattice-oxygen mediated mechanism, the formation of surface V_O (oxygen vacancies) is often resulted.^[6b, 7] As the leaching of cations act as one of the ways to compensate this process when the filling rate of OH^- (aq) to the surface V_O is not fast enough,^[7] it is common to detect catalyst surface amorphization over cycling.^[6a, 7] To examine the surface change of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ oxide particles after OER cycling, high-resolution transmission electron microscopy (HRTEM) images were collected. As can be observed, the cycled $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ particles show high crystallinity as that of the as-prepared ones (Figure 4c and Figure S15). We confirmed that the crystal structure of cycled

$\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ catalyst remain unchanged by XRD (Figure S16). In addition, the corresponding fast Fourier transforms (FFT) patterns (Figure 4c) can be indexed consistently to the corresponding bulk spinel structure. Thus, the excellent stability and a preserved high-crystalline surface over cycling indicate the low probability of lattice oxygen participation in spinel $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ during OER. Note that the lattice oxygen participation eventually leads to the formation of surface V_O ,^[6-7] the tendency of spinel oxide to have p-type conductivity might be the underlying reason inhibiting the lattice oxygen involvement. According to early reports, decreased formation energy of V_O is generally accompanied with dominating O 2p states near the Fermi and a smaller energy gap between O p-band center and Fermi level.^[7, 25] However, the investigated spinel models exhibit substantial metal 3d character near the Fermi level (Figure 3c, 3d). In addition, the energy of O p-band center relative to the Fermi level (~ -6.0 eV, Table S5) is much more negative than that of the identified oxygen-active perovskite catalysts (~ -2.0 eV),^[6b] further demonstrating the low activity of lattice oxygen in cation-deficient spinel oxides.

In summary, we have established a strong correlation between the Co-O covalency and the OER activity of substituted $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides. An enlarged Co 3d and O 2p covalency is found to be responsible for the activity enhancement brought by 10 ~ 30 at% Fe substitution as it facilitates the injection/extraction of electrons from oxygen. The best-performing $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ oxide serves as a promising low-cost electrocatalyst as it outperforms the benchmark IrO_2 catalyst and exhibits good cycling stability. While the pH-dependent OER activity of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ indicates decoupled proton-electron transfers during OER, the involvement of lattice oxygen is not considered as a favorable route. The cation-deficient spinel oxide gives a wide energy gap between the O p-band center and Fermi level and might hinder

the activation of lattice oxygen. Our work indicates that the metal-oxygen covalency bridges the fundamental understanding of OER by oxide catalysts with different defect chemistry. The new perspective from the cation-deficient chemistry enriches the existing mechanistic studies on spinel oxides towards electrocatalysis.

Supporting information

Supporting Information is available from the Wiley Online Library or from the authors.

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Figure 1. (a) XRD patterns of $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides. XANES spectra of $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ at (b) Zn (c) Fe and (d) Co K-edge. (e) Zn, Fe and Co valence states as a function of composition x in $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ oxides.

Figure 2. (a) The background correction and iR correction^[8a, 19] of OER CV curves performed in O₂-saturated 0.1 M KOH (scan rate: 10 mV s⁻¹, rotation speed: 1600 rpm). (b) OER specific activities of ZnFe_xCo_{2-x}O₄ ($x=0\sim 2.0$). (c) Potentials at 25 μA cm⁻²_{ox} for the spinel ZnFe_xCo_{2-x}O₄ ($x=0\sim 2.0$) catalysts. (d) Catalytic current retention (@ 1.65 V vs. RHE) of ZnFe_{0.4}Co_{1.6}O₄ over 5000 CV cycles in 0.1 M KOH, inset is the LSV curves of commercial IrO₂ and ZnFe_{0.4}Co_{1.6}O₄ in O₂-saturated 0.1 M KOH (scan rate: 10 mV s⁻¹, rotation speed: 1600 rpm).

Figure 3. (a) Molecular orbitals diagrams for the Co – OH (Co^{3+} , Co^{4+}) bonding at the surface of spinel oxides. (b) The OER activity, evaluated by the potentials at a current density of $25 \mu\text{A cm}^{-2}_{\text{ox}}$, as a function of parameter $N-V$. Computed partial electronic density of states (PDOS) of (c) ZnCo_2O_4 and (d) $\text{Zn}_V\text{-Fe-ZnCo}_2\text{O}_4$, inset are the corresponding DFT crystal models.

Figure 4. (a) CV of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ scanned in O_2 -saturated KOH (pH= 12.5~14) at a scan rate of 10 mV s^{-1} . (b) The overpotential (@ $50 \mu\text{A cm}^{-2}_{\text{ox}}$) and Tafel slope of $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ (at pH 14) compared with literature data.^[5b, 8a, 23] (c) HRTEM and FFT of as prepared $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$ powder and cycled electrode (50 cycles). (d) Illustration of decoupled proton-electron transfer of an exemplary rate-limiting step in the conventional OER mechanism (Figure S14).^[4a, 8a]

Table 1. The defect formation enthalpies ΔH_f under oxygen rich chemical potentials ($\mu_0 = 0$ eV). As a result of oxygen rich condition ($\mu_0 = 0$ eV), $\mu_{\text{Zn}} = -3.754$ eV.

	Calculated energy (eV)	ΔH_f (eV)
Zn_v (ZnCo₂O₄)	-301.753	1.515
O_i (ZnCo₂O₄)	-308.219	3.973
Zn_v (Fe-ZnCo₂O₄)	-304.100	1.376
O_i (Fe-ZnCo₂O₄)	-310.641	3.758

Metal-oxygen covalency has great implications for highly efficient spinel oxides towards oxygen evolution reaction (OER). An enlarged Co-O covalency by optimum Fe substitution in $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$ gives promoted OER superior to benchmark IrO_2 . Although the pH-dependent OER suggests non-concerted proton-electron transfers, the involvement of lattice oxygen is not considered favorable because of the downshifted O p-band center relative to Fermi level governed by the spinel's cation deficient nature.

Keywords: Metal-oxygen covalency; decoupled proton-electron transfers; cation deficiency; oxygen evolution reaction; spinel oxide

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Enlarged Co-O covalency in octahedral sites leading to highly efficient spinel oxides for oxygen evolution reaction