Solution Combustion Synthesis of Novel S,B-Codoped CoFe Oxyhydroxides for the Oxygen Evolution Reaction in Saline Water

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ABSTRACT: Green hydrogen presents itself as a clean energy vector, which can be produced by electrolysis of water by utilizing renewable energy such as solar or wind. While current technologies are sufficient to support commercial deployment of fresh water electrolyzers, there remain a few well-defined challenges in the path of commercializing direct seawater electrolyzers, predominantly related to the sluggish oxygen evolution reaction (OER) kinetics and the competing chlorine evolution reaction (CER) at the anode. Herein, we report the facile and swift fabrication of an S,B-codoped CoFe oxyhydroxide via solution combustion synthesis for the OER with apparent CER suppression abilities. The as-prepared S,B-(CoFe)OOH-H attained ultralow overpotentials of 161 and 278 mV for achieving current densities of 10 and 1000 mA cm⁻², respectively, in an alkaline saline (1 M KOH + 0.5 M NaCl) electrolyte, with a low Tafel slope of 46.7 mV dec⁻¹. Chronoamperometry testing of the codoped bimetallic oxyhydroxides showed very stable behavior in harsh alkaline saline and in neutral pH saline environments. S,B-(CoFe)OOH-H oxyhydroxide showed a notable decrease in CER production in comparison to the other S,B-codoped counterparts. Selectivity measurements through online FE calculations showed high OER selectivity in alkaline (FE ~ 97%) and neutral (FE ~ 91%) pH saline conditions under standard 10 mA cm⁻² operation. Moreover, systematic testing in electrolytes at pH values of 14 to 7 yielded promising results, thus bringing direct seawater electrolysis at near-neutral pH conditions closer to realization.

INTRODUCTION

Electrolysis of water has long been sought to be a sustainable and environmentally benign method of generating hydrogen (H₂) as an ever-promising future energy vector. The oxidative half-reaction at the anode, whereby molecular oxygen (O₂) is produced, has restrictively constrained water splitting applications to higher overpotentials due to sluggish kinetics of the 4e⁻ process and thermodynamically stable O–O double bond. To this extent, effective electrocatalysts have been developed to circumvent the constraints of the anodic oxygen evolution reaction (OER) via an array of catalyst groups, including, but not limited to, earth-abundant transition metal oxides (TMO), oxyhydroxides, nitrides, carbonaceous materials, phosphides, phosphates, selenides, and sulfides. Although notably different, the overarching goal inrationally designing these anodic electrocatalysts is to lower overpotentials through attaining surface and bulk electronic structure modulations, reducing charge transfer limitations, and enhancing intrinsic activity by exposing more active sites. Over the past few years, electrocatalysts with better water splitting performance compared to long-standing OER benchmark materials such as IrO₂ and RuO₂ have been reported. NiFe-based oxyhydroxides and layered double hydroxide (LDH) electrocatalysts have been among the most prominent OER anodes to date owing to their ultralow overpotentials, excellent durability, and cost-effective raw materials. However, significant work has been reported on cobalt-based electrocatalysts due to the favorable energetics atop the cobalt active sites for the alkaline and near-neutral OER.

Of interest toward reducing fresh and pure water needs in commercial electrolyzers, growing interest has been devoted to seawater as feed for electrolysis over the past few years. Seawater is undoubtedly the most copious aqueous electrolytic feedstock for electrolysis. However, a major challenge with direct seawater electrolysis is the presence of chloride (Cl⁻) ions. Anodically, a competing undesired chlorine evolution reaction (CER) occurs with lower kinetic hindrances due to the innately facile 2e⁻ transfer mechanism in generating hypochlorite (ClO⁻) or hypochlorous acid (HClO), depending on the pH of the electrolytic solution. Governed by the Pourbaix diagram, the highest probability of OER selectivity
can be realized under the so-called “alkaline design criteria,” whereby operating at or below ~480 mV anodic overpotential, irrespective of the corresponding current density, ensures that no CER occurs in alkaline conditions.

This overpotential window decreases as the pH decreases below 7.5. Furthermore, chloride corrosion of the electrode through the formation of an inert metal chloride-hydroxide surface is another challenge that is central to seawater electrolysis. It is worth noting that the primary cause of maintenance in commercial electrolyzers has been minor impurities found in the typical deionized buffered water feeds. Therefore, designing catalysts to operate in saline and seawater conditions will adventurously lead to advancement in catalyst designs toward pure water electrolysis.

Fundamentally, near-neutral pH conditions are key toward the viability of employing direct seawater electrolysis at a commercial scale. Attaining stable and commercially viable current densities at near-neutral pH conditions ensures curbing costly alkaline buffers during continuous operation and preventing Ca2+ and Mg2+ hydroxide precipitation due to pH gradients around electrodes in alkaline conditions. The latter has the potential to rapidly foul the membranes in conventional membrane-based electrolyzers and deactivate electrodes through depositing on the active sites. Thus far, the aforementioned challenges have proven difficult to address and alleviate simultaneously. However, a key design strategy is to ensure an ultraefficient alkaline OER followed by modifications for curbing the effects of the kinetically sluggish near-neutral pH electrolysis. Typically, it is of paramount importance to design near-neutral pH electrolytes with surfaces that have a strong water binding energy, which tends to be a major kinetically limiting step in the near-neutral OER mechanism.

Commercially feasible hydrogen production through water or seawater electrolysis is conditional upon attaining selective, continuous, and stable electrocatalyst/electrolyzer combinations operating at high current densities (≥500 mA cm−2) for rapid H2/O2 production.

Recently, a notable increase in interest has been directed toward the electrolysis of the saline electrolyte and seawater, aiming to curb the aforementioned challenges and achieve highly electroactive and stable electrocatalysts. For instance, Kuang et al. fabricated a multilayer anode consisting of a NiFe layer homogeneously coated on a porous NiS2 formed on Ni foam (NiFe/NiS2-Ni), which recorded an iR-compensated overpotential of ~300 mV for achieving 400 mA cm−2 of current density in alkaline saline water (1 M KOH + 0.5 M NaCl), well below the ~480 mV overpotential required for triggering hypochlorite formation through the CER. The same material attained a stable 1000 h of operation at an 870 mV overpotential for achieving the same 400 mA cm−2 of current density in alkaline seawater (1 M KOH + real seawater). XPS analysis indicated that polyanionic sulfite groups allowed for partial electrostatic shielding from bulk Cl−, thereby lowering the CER at larger potentials and suppressing chloride corrosion. Furthermore, Liang et al. very recently reported a core–shell structure composed of a conductive NiFe core and a thin amorphous NiFe oxyhydroxide shell array, which exhibited very low OER overpotentials of 248 and 258 mV in the alkaline electrolyte (1 M KOH) corresponding to current densities of 500 and 1000 mA cm−2, respectively. Facile Fe-doping was reported to significantly improve the performance through enhancing the electrochemically active surface area (ECSA) and improving conductivity. This is in good agreement with the findings of Anantharaj et al. on the effect that Fe-doping has on Co-based anodic catalysts. In their work, the so-called “Fe effect” was confirmed to facilitate the formation of electroactive amorphous oxyhydroxide layers with a larger exposed density of active sites. This enhances conductivity with respect to the Fe3+ content and modulates local electronics toward more facile OER kinetics. Moreover, S-doping of a binary metallic oxyhydroxide was recently shown to activate large current density operation through improved conductivity, hydrophilicity, and aerophobicity. In our recent work, we focused on developing cathodes for seawater electrolysis with intrinsically high activities in neutral pH operation and suppression of chloride-induced corrosion and deactivation. This was achieved on a novel NiV heterointerfaced oxide-nitride surface featuring electronic localization toward kinetically adsorbing and dissociating H2O and electrostatically repel Cl−. B-doping has been shown to also increase catalytic conductivity and modulation of OER intermediates’ binding energetics. Gupta et al. showed that a boron-rich shell atop a cobalt oxide core facilitates the formation of surface CoOOH groups, albeit low activities were recorded in neutral pH conditions. Modification to the electron density of Co sites through electronic correlation with the B-dopant can allow favorable Co2+ states, which are thermodynamically favored during the OER.

In this work, we have utilized the established solution combustion synthesis (SCS) method in initially fabricating a cobalt core. The resultant spinel cobalt oxide serves as both a core structure and provides active cobalt sites at the surface of an amorphous shell composed of bimetallic CoFe oxyhydroxide. Following this, in a single-step room-temperature process, we employed wet chemistry methods to provide surface Fe for the bimetallic oxyhydroxide shell and simultaneously codoped the oxyhydroxide with both sulfur and boron. S,B-codoping was intended to aid in tuning the valence state of Co/Fe, optimize the binding energies of OER intermediates, and increase the hydrophilicity for the near-neutral pH of OERs. Systematic parametric syntheses were undertaken to optimize the Co/Fe, Fe/S, and Co/B surface ratios. The optimal electrocatalyst with a Co/Fe molar ratio of 29:1, a Fe/S2 molar ratio of 14:1, and a weight ratio of Co/NaBH4 of 1:10 attained high activity in both alkaline (1 M KOH) and saline-alkaline electrolyte (1 M KOH + 0.5 M NaCl). This optimum material is hereby referred to as S,B-(CoFe)OOH-H. Furthermore, a parametric electrolyte study was conducted on different electrolytes with pH values varying from 7 to 14 to probe the catalytic performance for applications involving near-neutral pH, such as direct seawater electrolysis. Chronoamperometry (CA) testing was utilized to ensure stable performance for 50 h of operation in standard alkaline media, and a high alkalinity saline electrolyte (4 M KOH + 0.5 M NaCl) was undertaken to simulate harsh environments inducive of accelerated chlorine corrosion or catalyst poisoning. The formation of CER products from chloride oxidation was quantified using the established diethylphenylenediamine (DPD) method to investigate CER suppression of the oxyhydroxides during electrolysis of the neutral pH saline electrolyte. As such, CA testing was also performed in the neutral saline electrolyte to investigate the stability of the codoped oxyhydroxides under a relatively high potential of 1.7 V (vs reversible hydrogen electrode (RHE)) inducive of higher chloride corrosion. Selectivity measurements through online FE calculations showed high OER selectivity in alkaline (FE ~ 97%) and neutral (FE ~ 91%) pH conditions.
saline conditions under standard 10 mA cm$^{-2}$ operation. However, lower selectivity was registered under high current density (100 mA cm$^{-2}$) operation. Nevertheless, 50-h CA stability tests under a kinetically challenging neutral pH saline electrolyte showed stable performance at 10 and 100 mA cm$^{-2}$ for the novel S,B-codoped oxyhydroxides.

### RESULTS AND DISCUSSION

**Characterization.** A series of syntheses conducted through a rational variation of Fe and S precursors using a single-step codoping scheme were undertaken to tune the surface ratio of dopants on spinel cobalt oxide (Co$_3$O$_4$) synthesized through the solution combustion synthesis (SCS), shown in Scheme 1. The crystallinity and nature of the SCS cobalt oxide were confirmed through X-ray diffraction (XRD). Initial screening tests for catalyst activity has led to identifying the optimal S-(CoFe)OOH oxyhydroxide, which was further boronated in the same single-step to yield S,B-(CoFe)OOH-L or S,B-(CoFe)OOH-H, based on the Fe and S surface precursor ratios. The particle size distribution of the aforementioned samples (Figure S1) confirms that the bulk morphology is not significantly affected during progressive synthesis modulations by Fe-doping, sulfurization, and boronation. A morphological study of the as-synthesized oxyhydroxides was conducted through high-resolution transmission electron microscopy (HRTEM). Figures 1a and S2 present HRTEM images of the three main oxyhydroxides investigated herein. The surface roughness of the materials, as well as the prominence of the amorphous oxyhydroxide surface, is apparent to increase from S-(CoFe)OOH < S,B-(CoFe)OOH-L < S,B-(CoFe)OOH-H. Figure 1b depicts that the latter S,B-codoped oxyhydroxide appears to have the Co$_3$O$_4$ core support folded oxyhydroxide structures as well-rounded and thorough shells. Such homogenous and high surface area electroactive shells are known to substantially enhance OER activity through exposing a higher degree of electrochemically active surface area (ECSA). The HRTEM image of S,B-(CoFe)OOH-H, presented in Figure 1c, shows a clear distinct boundary between the crystalline Co$_3$O$_4$ core and the amorphous oxyhydroxide shell. Lattice fringe spacings of 0.245 and 0.457 nm correspond to the spinel cobalt oxide facets of (311) and (111), respectively. Furthermore, surface oxyhydroxides of the (100) CoOOH and/or (110) FeOOH phases are noted through a lattice fringe spacing value of 0.247 nm. Since the boronation step is conducted momentarily after the amorphic layer formation, a lattice spacing of 0.212 nm was found reciprocal to a Co$_2$B phase. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the corresponding EDS elemental mapping in Figure 1d convey how all corresponding elements in S,B-(CoFe)OOH-H are present and homogeneously dispersed in the electrocatalyst. The same analysis was conducted on S-(CoFe)OOH and is presented in Figure S3. Furthermore, FESEM/EDS in Figure S4 was conducted on S,B-(CoFe)OOH-H and the results indicate that the elemental composition of the material confirms the intended dopant ratios in the sample. The attained homogeneity is important for preventing phase separation during synthesis. Moreover, it is interesting to confirm the well-dispersion of cobalt in the amorphous oxyhydroxide layer—confirming that Co from the cobalt oxide core lattice migrates to the amorphous shell during synthesis.

XRD analysis was performed to confirm maintaining the crystalline spinel Co$_3$O$_4$ cores for the three investigated oxyhydroxides throughout the synthesis process. This is initially important to confirm that no changes occurred on
Figure 1. (a) HRTEM images of S-(CoFe)OOH, S,B-(CoFe)OOH-L, and S,B-(CoFe)OOH-H. (b) HRTEM images at a different magnification of the S,B-(CoFe)OOH-H showing the crystalline core—the amorphic shell boundary and highlighting the amorphous oxyhydroxide layer. (c) Lattice fringe spacing of S,B-(CoFe)OOH-H, and (d) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of S,B-(CoFe)OOH-H and the corresponding elemental mapping of Co, Fe, O, S, and B. (e) XRD patterns and (f) the corresponding varying degrees of blueshift of the dominant (311) phase in doped oxyhydroxides relative to core Co$_3$O$_4$. (g) Raman spectra of the as-prepared spinel Co$_3$O$_4$ (SCS), S-(CoFe)OOH, S,B-(CoFe)OOH-L, and S,B-(CoFe)OOH-H oxyhydroxides.
the favorable Co$_3$O$_4$ and that solely surface amorphization occurred relative to the control Co$_3$O$_4$ sample due to the growth of the oxyhydroxide layer during the secondary part of the synthesis. As can be seen in Figure 1e, the predominant (111) diffraction plane of spinel Co$_3$O$_4$ at 36.8° is present for all analyzed samples and further confirmed through HRTEM lattice fringe spacing in Figure 1c. Other peaks at 31.2, 38.5, 44.8, 55.6, 59.3, and 65.2° correspond to the (220), (222), (400), (422), (511), and (440) diffraction planes of Co$_3$O$_4$, respectively, are present and consequently indicate that the crystalline core purity of the electrocatalysts is maintained. Fe and nonmetallic S, B-codoping do not register a peak, which is preliminarily expected due to their low concentrations on the catalyst and noncrystalline structure on the surface. Furthermore, clear peak distortions in the form of peak intensity reductions, subtle blueshifts, and increases to the full-width at half maximum (FWHM) become present upon doping Co$_3$O$_4$ cores. To this end, increased FWHM and notable blueshifts in the predominant (111) peak, shown in Figure 1f, indicate subtle textural changes that are expected due to oxyhydroxide layer growth on crystalline cores. The largest recorded blueshift by 0.21° for the S,B-(CoFe)OOH-H suggests a high degree of lattice strain due to amorphization effects. A possible reason for this can be inferred from differences in ionic radii and oxidation state distribution between dopant Fe and surface Co on the oxyhydroxide surface, which may result in surface interactions causing distortions most reflected on the main exposed facets of the underlying crystalline core. Nevertheless, it has recently been reported that modulation of intermediate adsorption energies for more thermoneutral theoretical OER overpotentials can be achieved through appropriate lattice distortions, including, but not limited to, compressive strains exhibited here due to amorphization and doping. HRTEM images of Figure 1a confirm that S,B-(CoFe)OOH-H attained the highest degree of oxyhydroxide growth and consequently the largest degree of surface amorphization effects. Moreover, Raman spectroscopy was undertaken, as presented in Figure 1g, to further confirm structural strains attained upon S,B-codoping. In the scanned range of 40–1200 cm$^{-1}$, the prominent Raman peaks for the base cobalt oxide shell (i.e., Co (SCS)) prepared under the solution combustion synthesis (SCS) correspond to the spinel Co$_3$O$_4$ structure. Peaks at 683, 612, 517, and 479 cm$^{-1}$ conform to the A$_{1g}$, E$_{2g}$, and E$_g$ modes of crystalline Co$_3$O$_4$, albiet with a notable red shift of approximately 4–9 cm$^{-1}$ in all peaks. Such red shifts may correspond to an initially distorted lattice of the Co$_3$O$_4$, potentially as a result of the ultrafast crystallization time endured under the SCS. Moreover, we note a secondary red shift of the dominant A$_{1g}$ peak at 683 cm$^{-1}$ between the S-doped and S,B-codoped oxyhydroxides. We hypothesize that the overall ratio of surface sulfur and boron doping facilitates lattice straining causing red shifting. Moreover, upon undertaking a Lorentzian fit on the highlighted peaks, we observe peak broadening and a clear decrease in peak intensity, which are suggestive of an increased degree of lattice strain and amorphization. An increase of the FWHM in the A$_{1g}$ mode is evident as the degree of oxyhydroxide doping (i.e., boron and sulfur dopants) increases, leading to a maximum FWHM of the S,B-(CoFe)OOH-H sample, which is indicative of possible oxygen vacancies. X-ray photoelectron spectroscopy (XPS) analysis was performed to examine the chemical states of surface elemental

Figure 2. (a) Deconvoluted XPS spectra of Co 2p, (b) Fe 2p, (c) O 1s, (d) S 2p, and (e) B 1s for S-doped and S,B-(CoFe)OOH oxyhydroxide samples.
orbitals, respectively, and their analogous 2p1/2 spin orbitals at 795.6 and 797.8 eV. Moreover, an increased ratio of Co2+/Co3+ is found to be present in the better performing S,B- to the S-doped oxyhydroxide. Some dielectronic correlation between the Co and Fe centers relative to the S-doped oxyhydroxide. This conveys the regulating effect of B-doping since OER efficiencies peak OD1 and OD2, whereby lower coordination oxygen bound to higher valence state Co/Fe is expected in the OD2 peaks.

Figure 3. (a) Polarization curves, (b) corresponding Tafel plots, and (c) linear sweep voltammetry (LSV) curves before and after 1000 cyclic voltammetry (CV) cycles for S-(CoFe)OOH, S,B-(CoFe)OOH-L, and S,B-(CoFe)OOH-H in alkaline (1 M KOH) conditions. (d) Plot of electrochemically active surface area (ECSA) vs double-layer capacitance (Cdl) and (e) EIS Nyquist plots of the as-prepared oxyhydroxides. (f) Comparison of polarization curves of the S-doped and B,S-codoped (CoFe)OOH in alkaline (solid lines) and saline-alkaline (dotted lines) conditions. Saline-alkaline (1 M KOH + 0.5 M NaCl) plots were recorded after 25 h of chronoamperometry at 50 mA cm−2 of current density.

Figure 2d presents the deconvoluted S 2p peaks and shows higher amorphic surfaces, and consequently, resulted in larger linewidth, or FWHM, of Co 2p spectra, whereby deconvolution of S-(CoFe)OOH shows peaks at binding energies of 780.2 and 781.8 eV corresponding to the Co3s and Co2s 2p3/2 spin orbitals, respectively, and their analogous 2p1/2 spin orbitals at 795.6 and 797.8 eV. Moreover, an increased ratio of Co3+/Co3s is found to be present in the better performing S,B-codoped catalysts, especially the optimum S,B-(CoFe)OOH-H. This conveys the regulating effect of B-doping since active cobalt with low oxidation state Co2+ accelerates the corresponding shifting points toward a stronger electronic correlation between the Co and Fe centers relative to the S-doped oxyhydroxide. Some differences in the linewidth, or FWHM, of fitted peaks for Fe 2p, and Co 2p to a lower extent, are noted. FWHM may widen due to a local increase in the neighboring chemical bonding states, indicative of a higher degree of amorphicity. This is in fact expected for the boronated oxyhydroxides in particular, which exhibited boronated oxyhydroxides, with no presence of residual impurities from synthesis recipes. Figure 2a shows the high-resolution Co 2p spectra, whereby deconvolution of S-(CoFe)OOH shows peaks at binding energies of 780.2 and 781.8 eV corresponding to the Co3s and Co2s 2p3/2 spin orbitals, respectively, and their analogous 2p1/2 spin orbitals at 795.6 and 797.8 eV. Moreover, an increased ratio of Co3+/Co3s is found to be present in the better performing S,B-codoped catalysts, especially the optimum S,B-(CoFe)OOH-H. This conveys the regulating effect of B-doping since active cobalt with low oxidation state Co2+ accelerates the conventionally rate-limiting third electron-transfer process (M−O + OH− → M−O−OH + e−). As will be discussed later, the S,B-(CoFe)OOH-H oxyhydroxide showed superior performance, which to some degree can be attributed to the larger concentration of Co2s to Co3s, relative to the S,B-(CoFe)OOH-L oxyhydroxide. Three satellite peaks labeled “Sat.” were identified as representative of expected cobalt-oxygen species. Similarly, the fitted Fe 2p spectra in Figure 2b shows the expected Fe3s and Fe2s peaks and their corresponding satellites. Interestingly, a notable blue shift toward higher binding energy is observed between the reference S-(CoFe)OOH and the S,B-(CoFe)OOH-L for both Co3s and Fe3s peaks by approximately 0.33 and 1.74 eV, respectively. This effect is less apparent between the reference S-doped oxyhydroxide and the S,B-(CoFe)OOH-H, with shifts of 0.21 and 1.23 eV in the Co3s and Fe3s peaks, respectively. The aforementioned shifting points toward a stronger electronic correlation between the Co and Fe centers relative to the S-doped oxyhydroxide. Some differences in the linewidth, or FWHM, of fitted peaks for Fe 2p, and Co 2p to a lower extent, are noted. FWHM may widen due to a local increase in the neighboring chemical bonding states, indicative of a higher degree of amorphicity. This is in fact expected for the boronated oxyhydroxides in particular, which exhibited higher amorphic surfaces, and consequently, resulted in larger differences in FWHM for the S,B-codoped catalysts. Figure 2c presents the deconvoluted O 1s spectra showing three notable peaks at 529.8, 530.3 (or 531.1 for boronated samples), and 532.1 eV corresponding to lattice oxygen (O M) in spinel Co3O4, defective or low coordination oxygen from M-OOH (O D1 or O D2), and physi- or chemisorbed oxygen functionalized species (O B, i.e., sulfates and/or water). Boronated samples show a blue shift toward higher binding energy in the oxygen deficiency peak O D1 and O D2 whereby lower coordination oxygen bound to higher valence state Co/Fe is present in the OD1 peaks.

Figure 2d presents the deconvoluted S 2p peaks and shows leading difference between the S-doped oxyhydroxide and its S,B-codoped counterparts. The S-(CoFe)OOH sample exhibits a peak at 162.3 eV corresponding to S 2p3/2 indicative of M−S bonds and a secondary shoulder peak reflective of surface SO2−. In contrast, the S,B-codoped oxyhydroxides have been fitted with two additional peaks at higher binding energies of 164.1 and 167.6 eV reciprocal of the S 2p3/2 (low coordinated surface sulfur) and surface SO2−, respectively. Moreover, the latter S−O peaks seem to increase in area, as the M−S peaks decrease between the -L and -H oxyhydroxides. This indicates that the higher Fe ratio on the surface in S,B-(CoFe)OOH-L allows further oxygen coordination with sulfur, compared to the S,B-(CoFe)OOH-H sample, which has a higher exposed Co ratio favoring Co-S and Co-B bonds. Shifting to a higher binding energy is witnessed for the corresponding OD1 peaks.

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density shifts from B to surface Co and/or Fe sites, highlighting a strong electronic correlation between the dopant and active catalytic sites. Furthermore, as mentioned previously, regulating the oxidation state of Co\(^{4+}\) is quite advantageous for the OER, which is partially facilitated through boronation. This is because the Co\(^{3+}/Co^{4+}\) transition is more thermodynamically facile than the Co\(^{3+}/Co^{4+}\) transition.

**Alkaline Saline Water Oxidation.** The performance of the catalysts was initially screened in the alkaline electrolyte (1 M KOH) before synthesis optimization, and testing in the saline electrolyte was undertaken. Figure 3a depicts the polarization curves of the three central oxyhydroxides reported herein (S-(CoFe)OOH, S,B-(CoFe)OOH-L, S,B-(CoFe)-OOH-H), and conventional benchmark IrO₂/C. As mentioned previously, an array of only S-doped oxyhydroxides with different Co/Fe and Fe/S ratios was fabricated and tested. However, for brevity of focus on S,B-codoped samples, the S-(CoFe)OOH catalysts exhibited the lowest overpotential (341 mV at 10 mA cm\(^{-2}\)) compared to the latter. ECSA calculations were determined by identifying the double-layer capacitance (\(C_{dl}\)). The latter point makes this fabrication method more lucrative especially at higher current densities when bubble formation is rapid. At this regime, bubble releases away from the catalytic surface, a function of the catalyst’s aerophobicity, and is as influential on performance as electrolytic diffusion to active sites.\(^6\) Electrochemical impedance spectroscopy (EIS) was also used to probe the kinetics of the as-prepared catalysts, as demonstrated from the Nyquist plots in Figure 3c. S-(CoFe)OOH-H shows the smallest charge transfer resistance (\(R_{ct}\)) at 0.92 \(\Omega\), which is almost 14 times more conductive than the S-doped counterpart. Thus, it appears that the incorporation of boron to S-doped samples enhances conductivity to a large degree, possibly due to the different amorphic surface chemistry, which promoted a larger degree of oxygen deficiencies in the S,B-codoped catalysts as shown by XPS. This can be translated to lower interfacial resistances at the catalyst—electrolyte interface, which lower the effective \(R_{ct}\). Oxygen defects, found in the S,B-codoped sample, have been previously reported to enhance conductivity in similar electrocatalytic systems through density functional theory (DFT) studies, showing a decrease in energetic separation between the M 3d and O 2p band centers.\(^5\) This decreased energetic separation is known to enhance conductivity and modulation of surface electronics toward enhancing kinetics of the 4e\(^-\) transfer OER process, as confirmed through Tafel slopes in Figure 3b. Furthermore, optimized oxygen vacancy concentrations were found to optimize the electronic structure, consequently increasing the rate of electron transmission and the 4e\(^-\) OER process.\(^5\)

It is important to probe the catalytic surface’s affinity for OER selectivity, relative to the CER, and bring forth methods that enable OER selectivity enhancements without diminishing electrolytic performance.\(^6\) We tested our materials in synthetic alkaline saline water (1 M KOH + 0.5 M NaCl) to evaluate the selectivity of the catalysts toward the OER versus the CER during the electrolysis of seawater. Figure 3f shows polarization curves of the catalysts in the alkaline (1 M KOH) electrolyte (solid lines) and the corresponding polarization curves after 25 h of chronoamperometry in saline-alkaline (1 M KOH + 0.5 M NaCl) conditions (dotted lines). Interestingly, the presence of a boron-sulfur-doped amorphous shell works favorably in improving alkaline saline performance. The S-doped sample showed an increase in the overpotential in the alkaline saline electrolyte, possibly due to chloride-corrosion partially passivating active sites through the metal-chloride formation.\(^5\)

The optimum S,B-(CoFe)OOH-H oxyhydroxide sample in alkaline saline conditions (1 M KOH + 0.5 M NaCl) attains iR-corrected current densities of 10, 100, and 1000 mA cm\(^{-2}\) at ultralow overpotentials of 161, 198, and 278 mV, respectively. This is in good agreement with the same catalyst’s performance in nonsaline alkaline conditions. It can be qualitatively deduced that since both polarization curves in alkaline and saline-
alkaline electrolytes match after 90% iR correction, the S,B-(CoFe)OOH-H achieves good stability in the saline electrolyte and consequently good resistance toward chloride-induced corrosion. Since both S-(CoFe)OOH and S,B-(CoFe)OOH-H were fabricated under the same Fe and S dopant ratios relative to the underlying Co, it can be deduced that the predominant activity and chloride-induced deactivation resistance is due to the boronation step. Referring to S 2p and B 1s spectra in Figure 2d,e, we note that S,B-(CoFe)OOH-H contains the highest degree of surface S,B-polyanionic species, which electrostatically shield the buried catalyst from the Cl$^-\$ content. Coupling this with the larger ECSA for this material relative to its unboronated counterpart, a thicker homogeneously covered shielding oxyhydroxide layer helps in suppressing chloride transmission to active sites. Similar recent work by Li et al. showed that an anodic NiFeB$_x$ interlayer suppresses chloride corrosion through shielding the catalyst architecture from chloride propagation.

Figure 4a summarizes some of the most prominent OER electrocatalysts in alkaline electrolytes, whereby clearly a trend is noted pertaining to the importance of doping oxyhydroxides using S and B species. Moreover, it is clear from the figure that our materials show a remarkable decrease in overpotentials with respect to progressive modulation. Furthermore, the B,S-(CoFe)OOH-H oxyhydroxide catalyst proves to be among the most electroactive anodic catalysts designed to date for alkaline water oxidation. Figure 4b depicts the stable performance of both B,S-(CoFe)OOH catalysts in the alkaline electrolyte (1 M KOH). However, a slight degradation of the S-doped oxyhydroxide is witnessed after 24 h of operation at a constant current density of 10 mA cm$^{-2}$. To some extent, this may be a result of the min chipping of the drop-casted active catalyst on the GCE, which was visible at the end of the CA test. The promising performance of both S,B-codoped samples motivated similar CA testing under the same potentiostatic conditions in the alkaline saline (1 M KOH + 0.5 M NaCl) and accelerated decay saline-alkaline environment (4 M KOH + 0.5 M NaCl) at a constant current density of 10 mA cm$^{-2}$.

**Near-Neutral Saline Water Oxidation.** Although not necessarily the case, the more electroactive a catalyst is in alkaline conditions, the better it performs in neutral and near-neutral pH environments. This should not be taken as the sole catalyst design strategy, as other factors such as surface energetics toward water binding can significantly hinder activity in neutral pH operation. Therefore, targeting near-neutral pH conditions for electrolysis of saline electrolyte and seawater, we systematically tested both the S-doped (CoFe)-OOH and the S,B-(CoFe)OOH-H oxyhydroxides in an array of electrolytes under different electrochemical conditions. Figure 5a,b reports the overpotentials attained for S-(CoFe)-OOH and S,B-(CoFe)OOH-H, respectively, at a current density of 300 mA cm$^{-2}$, unless otherwise specified as in the case with bicarbonate and phosphate buffer testing. All reported overpotentials are attained upon performing 90% iR corrections using the respective R$^s$ values from EIS Nyquist plots for each electrolytic system—presented in Table S8.

Figure 4. (a) Comparison of overpotentials (mV) at 10 mA cm$^{-2}$ for the recently reported high-performing OER electrocatalysts in alkaline water splitting and the three main oxyhydroxides discussed in this work.63−74 (b) Long-term chronoamperometry in alkaline (1 M KOH) conditions at a constant current density of 50 mA cm$^{-2}$. (c) Long-term stability tests for B,S-(CoFe)OOH-H in conventional saline-alkaline (1 M KOH + 0.5 M NaCl) and accelerated decay saline-alkaline environment (4 M KOH + 0.5 M NaCl) at a constant current density of 10 mA cm$^{-2}$.

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Numerical values of said overpotentials in different electrolytes during S- and S,B-codoped oxyhydroxide testing are listed in Table S9, and corresponding polarization curves are presented in Figures S6 and S7.

Generally, a trend is evident whereby as the electrolyte’s pH decreases, approaching neutrality, the required overpotential to obtain the same current density increases. This is expected as oxyhydroxides are intentionally designed for improving surface energetics of the OH* binding strength for the OER mechanism in alkaline media. A spH decrease substantially decreases as well, in turn presenting kinetically limited electrolysis environments for the anodic OER. The outlier overpotential value for S-(CoFe)OOH in 1 M carbonate (pH = 12) may be due to some yet obscure mechanism between oxyhydroxides and carbonate electrolytes. The same can be presumed for the overpotential value of S,B-(CoFe)OOH-H in 1 M PB (pH = 7). Notwithstanding, as expected, increasing electrolytic concentration to 2 M allows for a clear overpotential drop, which can be attributed to the enhanced mass transport efficiencies proportional to the increased conductivity of the electrolyte solution. The concentration gradient between hydroxide ions and water molecules as pH approaches neutrality allows for water molecules to be the initial reaction intermediate in the OER mechanism. The drastic difference in performance between the S-doped and S,B-codoped oxyhydroxides at near-neutral pH conditions is indicative of superior H2O adsorption upon boron doping. The reaped benefits of attaining a relatively low overpotential of 467 mV at a current density of 300 mA cm−2 in saline bicarbonate buffer (2 M Bicarbonate + 0.5 M NaCl) presents itself as an opportunity for direct natural seawater splitting without the consequences of the CER since this overpotential is below the 480 mV thermodynamic limit for the CER. Furthermore, carbonate-based buffers are highly desirable toward CO2 sequestration. Moreover, the utilization of a metallic substrate like Ni or Co foam under these conditions is believed to enhance the performance further.

An important point to note is that although under neutral saline conditions (1 M PB + 0.5 M NaCl), the required overpotential to initiate the chlorine evolution reaction (CER) is the thermodynamic limit (ηCER,lim) required overpotential of ~470 mV (1.70 V (vs RHE)), pH drops at the anode surface because proton generation lowers the ηCER,lim further. This motivated us to undertake a stringent investigation in quantifying CER products at overpotentials of 470 mV in the
3-electrode cell. We conducted 6-h CA studies in neutral saline conditions while quantifying the formation of chloro-reaction products. Under the near-neutral pH regime investigated, we expect the generation of hypochlorous acid (HClO), which is detectable and quantifiable via the standard DPD method. This study was not performed at higher potentials for the main reason. Essentially, the ultra-active S,B-codoped oxyhydroxides allow the OER to progress at a very high rate atop the GCE when operating at potentials exceeding 1.70 V (vs RHE). This caused massive bubble formation, which may mechanically etch the catalyst from the GCE surface after some hours of operation. This reason, coupled with the thermodynamically allowable generation of CER products, which was observed from DPD measurements, motivated us to perform the aforementioned stability studies at a potential of 1.70 V (vs RHE). However, it is highly recommended to perform similar tests at higher potentials if a metallic substrate is employed for a binder-free catalyst. Appropriating the DPD method for CER product quantification, we registered 1.01 and 0.74 mg/L of HClO at the end of the 6-h CA study on S,B-(CoFe)OOH-L and S,B-(CoFe)OOH-H, respectively. Correspondingly, the rate of CER production can be taken to be 0.168 and 0.123 mg/L (h). The results are summarized in Figure 5c. Although both catalysts show competitive CER and disadvantageously favor electrolyzer operation at lower potentials to prevent toxic chloro-reaction product formation, a clear selectivity toward the OER is apparent for the S,B-(CoFe)OOH-H oxyhydroxide.77 The highly hydrophilic amorphous layer of the S,B-(CoFe)OOH-L oxyhydroxide aids in capturing a higher flux of water molecules (for the OER) than chloride ions (for the CER). Furthermore, the anionic S- and B-codoped species atop the oxyhydroxide may electrostatically shield a degree of negatively charged Cl from reaching the catalytic surface, in effect suppressing the CER. This is postulated based on the higher degree of amorphous coverage atop the S,B-(CoFe)-OOH-H relative to S,B-(CoFe)OOH-L, whereby the former exhibited more selective OER performance. Prominent work in recent years involving applications of passive and permselective overlayers for CER suppression can be investigated to ascertain whether high-performing anodic electrocatalysts, as presented, will require further innate structural and design modifications.22 Operation at a relatively high potential of 1.70 V (vs RHE) in a neutral saline electrolyte proved to attain high-performance stability, through which the current density of the S,B-(CoFe)OOH-H catalyst dropped by less than 1% after 6 h of operation.

Moreover, Figure 5d shows 50-h stability tests performed for S,B-(CoFe)OOH-L and S,B-(CoFe)OOH-H catalysts drop-casted on porous nickel foam (NF) as a substrate. Chronoamperometry (CA) stability testing was performed in the same neutral pH saline electrolyte and under 1.56 and 1.73 V (vs RHE) corresponding to the required applied potentials to achieve current densities of 10 and 100 mA cm2, respectively, for the top-performing S,B-(CoFe)OOH-H anode. At 10 mA cm2, negligible decreases in current densities of 1.1 and 0.7% were recorded for S,B-(CoFe)-OOH-L and S,B-(CoFe)OOH-H, respectively. Correspondingly, drops of 5.2 and 4.8% in current density were registered for S,B-(CoFe)OOH-L and S,B-(CoFe)OOH-H, respectively. These results indicated that both S,B-codoped samples are quite stable in neutral pH saline electrolytes. We believe that the mutual stability in performance arises from the same effective surface heterojunctions of dopants to the spinel Co3O4 cores since the same synthesis procedure was employed for both catalysts. Furthermore, it is known that drop-casting has the intrinsic limitation of producing artificial drops in performance due to the etching or lamination effects of the catalyst powder from the underlying substrate. Thus, for future work, we propose growing the catalytic surface directly on the NF support to ensure heterojunctions between the catalyst and the substrate, which should eliminate catalyst powder etching or lamination effects. To this end, the ~1% drop in performance after 6 h in the neutral pH saline electrolyte, shown in Figure 5e, is partially due to performing the CA tests at elevated current densities using catalysts drop-casted on the GCE, whereby bubble-formation effects can more easily hinder mechanical stability of the catalyst powder on the GCE. A brief morphological characterization was performed on S,B-(CoFe)-OOH-H using FESEM after 10 CV cycles in alkaline, saline-alkaline, neutral, and saline neutral pH electrolytes, as shown in Figure S8. As can be determined, no discernable morphological changes (i.e., agglomeration or surface textural features) can be inferred to have occurred post-OER relative to pre-OER morphology (Figure S4). This aids in explaining the stable electrocatalytic performance attained.

Furthermore, to quantitatively probe catalyst selectivity toward the OER in the saline electrolyte, we performed Faradaic efficiency (FE) measurements at 1-h intervals during CA testing. Two sequential 6-h CA tests were performed under alkaline pH saline and neutral pH saline electrolytes, respectively. For each experiment, CA was maintained at a potential corresponding to 10 mA cm2 for 3 h followed by 100 mA cm2 for the remaining 3 h, as shown in Figure 5e,f. The FE results at low current densities of 10 mA cm2 are quite high, being approximately 97% for alkaline pH saline and 91% for neutral pH conditions. It is worth noting that for both pH conditions investigated, an increase in FE is witnessed after the first hour followed by a slight decrease, potentially due to initial electro-activation phenomena followed by microbubble-catalyst interfaces creating larger interfacial resistances.78,79 Upon increasing the current density to a larger value of 100 mA cm2, FE drops. However, a quick recovery in FE is observed in alkaline pH saline, whereby in the first hour at a current density of 100 mA cm2 operation, the FE is 78% and then increases to 89% in the third hour. Although the same trend is present for neutral pH saline operation at a high current density, the drop in FE after the first hour at 100 mA cm2 is more significant (42%) and the recovery is more subtle, reaching 48% at the final hour. These results can be explained by the low overpotential requirements under alkaline conditions, relative to the neutral pH environments, whereby the applied overpotential in the former at 100 mA cm2 is below the CER thermodynamic limit, and thus no CER products are expected to form. In contrast, under neutral pH saline conditions, an overpotential of 500 mV was required to achieve 100 mA cm2, which is larger than the CER thermodynamic limit.

In summary, based on the obtained performance and characterization results for the investigated S-doped and two S,B-codoped oxyhydroxides, we can draw clear conclusions pertaining to the individual functional effects Fe, S, and B have on activity, kinetics, stability, and selectivity. The combination of a higher Co to Fe (29:1) and Fe to S (14:1) ratios in S,B-(CoFe)OOH-H, relative to S,B-(CoFe)OOH-L, displayed itself in notably higher activities and kinetics. The lower amount of doped Fe and S in the optimum sample presented a
larger secondary amorphous oxyhydroxide phase and ECSA, as shown in Figures 1a and 3d, respectively. This effectively increases the surface density of active sites available for the reaction on this material, therefore allowing higher current densities to be realized. Furthermore, Nyquist analysis showed the highest conductivity for S,B-(CoFe)OOH-H, which explains that more favorable OER kinetics were achieved relative to S,B-(CoFe)OOH-L. The increased conductivity is most probably due to the larger Fe$^{3+}$ content on the more conductive sample, as shown in Figure 2b. Thus, lowering Fe-doping was found to facilitate more Fe content to be in the conductive Fe$^{3+}$ state while simultaneously favoring a larger desired ratio of Co$^{2+}$/Co$^{3+}$. Improvements in hydrophilicity, conductivity, and also ECSA size are achieved through S-doping, which translates to enhanced activities and kinetics, relative to the standalone undoped catalyst.$^{32}$ The final boronization step can best be clarified by comparing S-(CoFe)OOH and S,B-(CoFe)OOH-H, which were synthesized with the same ratio of Fe and S. The very notable improvement in performance for the boronated sample can be attributed to the regulating effect boron has on the surface metallic character through strong electronic correlation that is confirmed from shifting of B 1s spectra, as shown in Figure 2e. Moreover, contact angle measurements for the two samples shown in Figure S9 convey the improved hydrophilicity for the boronated sample, which translates to faster kinetics, especially in neutral pH conditions. Theoretical DFT investigations on both S and B-doping indicated electronic modulation of the active metal sites for the OER and predicted enhanced conductivities by decreasing energetic separation between band centers of metallic 3d and oxygen 2p.$^{57}$ Furthermore, and conducing Fe$^{3+}$ state while simultaneously favoring a larger desired ratio of Co$^{2+}$/Co$^{3+}$. Improvements in hydrophilicity, conductivity, and also ECSA size are achieved through S-doping, which translates to enhanced activities and kinetics, relative to the standalone undoped catalyst.$^{32}$ The final boronization step can best be clarified by comparing S-(CoFe)OOH and S,B-(CoFe)OOH-H, which were synthesized with the same ratio of Fe and S. The very notable improvement in performance for the boronated sample can be attributed to the regulating effect boron has on the surface metallic character through strong electronic correlation that is confirmed from shifting of B 1s spectra, as shown in Figure 2e. Moreover, contact angle measurements for the two samples shown in Figure S9 convey the improved hydrophilicity for the boronated sample, which translates to faster kinetics, especially in neutral pH conditions. Theoretical DFT investigations on both S and B-doping indicated electronic modulation of the active metal sites for the OER and predicted enhanced conductivities by decreasing energetic separation between band centers of metallic 3d and oxygen 2p.$^{57}$ Furthermore, and of particular interest toward OER stability in saline electrolytes, sulfur and boron polyatomic character confirmed through XPS aids in providing an electrostatically shielding layer from bulk Cl$^-$. This phenomenon limits Cl$^-$ from reaching the buried catalyst interface, thereby suppressing undesired chloride-induced deactivation and corrosion phenomena. Correlating the more polyatomic S,B-codoped surface of S,B-(CoFe)-OOH-L relative to S-(CoFe)OOH with respect to stability in the alkaline pH saline electrolyte (Figures 3f and 4b), we note that chloride deactivation is suppressed due to more effective Cl$^-$ electrostatic shielding. Similarly, the higher degree of polyatomic S,B-species in S,B-(CoFe)-OOH-H relative to S,B-(CoFe)-OOH-L, shown by XPS, results in improved selectivity, as shown in Figure 5c.e. Therefore, the combined effects of appropriate doping of Fe, S, and B results in optimized ECSA, conductivity, surface energetics toward OER intermediates, hydrophilicity, and CER suppression.

There are presently two utilized mechanisms for describing the OER, namely, the adsorbate escape mechanism (AEM) and lattice oxygen oxidation mechanism.$^{80,81}$ Pertaining to the conventional AEM, the OER is ensured through multiple adsorbed intermediates with correlated adsorption energies.$^{82}$ Wang et al. reported that CoOOH for the OER proceeds under the governance of the aforementioned AEM, whereby the minimum theoretical overpotential for the AEM is greater than 370 mV.$^{80}$ Although the S,B-(CoFe)OOH-H oxyhydroxide comprised active CoOOH and FeOOH sites, the ultralow overpotentials attained, especially in alkaline media, are more probably due to lattice oxygen migration (LOM) activation in alkaline media and due to the incorporation of boron and sulfur doping of the oxyhydroxide. We arrive at this outcome after verifying that metal-site oxidation peaks are not present at the end of the electro-activation cycles for the optimum codoped CoFe catalyst (Figure S10). The codoping strategy optimizes the local coordination environment and electronic structure resulting from the microengineered amorphous layer, whereby M−O$\cdot$OH, (i.e., M is Co, Fe) is the catalytic species for the OER under the LOM. Seeing as the base system for our material is effectively a Co oxyhydroxide (CoOOH), doping of Fe, S, and B, and enhancing OER activity may well be a synergistic contribution of both mechanisms.

CONCLUSIONS

This work demonstrates a swift and facile synthesis method composed of an initial step attaining cobalt oxide cores in large batches and a single-pot wet chemistry tri-doping strategy undertaken at room temperature in mere minutes. The bimetallic (CoFe) S,B-codoped oxyhydroxide fabricated under this method achieved ultralow overpotentials of 161 and 278 mV for achieving current densities of 10 and 1000 mA cm$^{-2}$ in the alkaline saline (1 M KOH + 0.5 M NaCl) electrolyte. This corresponded to a low Tafel slope of 47.6 mV dec$^{-1}$, indicating facile kinetics. Characterization techniques such as HRTEM and XPS show a homogenous dispersion of dopants throughout the oxyhydroxide—in effect curbing disadvantages of phase separation phenomena. XRD, Raman, and electrochemical measurements confirm a high ECSA for the optimum S,B-(CoFe)OOH-H electrocatalyst. Ideal Fe$^{3+}$ and Co$^{2+}$ character in the best-performing anode result in accelerated conductivity and activity, respectively. Boronation was found to facilitate the formation of high ECSA secondary amorphous oxyhydroxide phases, modulate a lowering in O 2p and metal 3d band centers to improve conductivity, enhance hydrophilicity, and electronically regulate surface metallic sites. We have investigated the effects of S,B-codoping on CER suppression when operating at an overpotential of 470 mV, which is at the thermodynamic limit for triggering CER in neutral pH conditions. However, CER products were generated and quantified due to local pH drops near the anode during high rate OER operation at these conditions. Through DPD measurements, we quantified a notable lowering of chloro-reaction species between the two S- and B-codoped oxyhydroxide, whereby S,B-(CoFe)OOH-H exhibited a higher CER suppression ability. Selectivity measurements through online FE calculations showed high OER selectivity in alkaline (FE $\sim$ 97%) and neutral (FE $\sim$ 91%) pH saline conditions under standard 10 mA cm$^{-2}$ operation. However, lower selectivity was registered under high current density (100 mA cm$^{-2}$) operation. A 50 h chronoamperometry stable performance at current densities of 10 and 50 or 100 mA cm$^{-2}$ was achieved in alkaline and neutral saline electrolytes, respectively, mimicking seawater. A systematic parametric study on the S-doped and S,B-codoped oxyhydroxides was also undertaken in electrolytes at different pH values covering from alkaline to neutral conditions, with and without the addition of NaCl to mimic seawater. The codoped species shows resilience in all tested conditions and offers routes for utilization at different electrolytic conditions. All in all, the fabricated S,B-(CoFe)OOH-H electrocatalyst outperformed other contemporary materials due to a large electrochemical active surface area (ECSA), low charge transfer resistances facilitating rapid kinetics, apparent hydrophilicity for enhanced mass transport, and stable performance in harsh environments for accelerated degradation. Commercially demanded current densities have...
been achieved, and the incorporation of metallic substrates for enhanced kinetics at near-neutral pH saline conditions are expected to result in higher activities, stronger heterojunction, and lower charge transfer resistances for industrial realization. We believe that the rational design, synthesis, and testing strategy undertaken in this work should aid in paving the way for a wider net of performance testing criteria for the multitude of reported OER electrocatalysts. Our strategy can be applied to other three-dimensional (3D) multilaminar systems, other bimetallic and trimetallic oxyhydroxides, which may result in better performances at near-neutral saline conditions.

**EXPERIMENTAL SECTION**

**Chemicals and Materials.** Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, analytical reagent), iron(II) nitrate nonahydrate (Fe(NO₃)₂·9H₂O, analytical reagent), cobalt acetate (Co(CH₃CO₂)₂, glycine (C₂H₅NO₂, analytical reagent) urea (CO(NH₂)₂), potassium hydroxide (KOH), and isopropyl alcohol (C₃H₈O, analytical reagent) were all purchased from Alfa Aesar. Throughout all experiments, deionized water was acquired the desired molar concentrations of aqueous KOH solutions. Sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O) sodium borohydride (NaBH₄) were purchased from Alfa Aesar. Throughout all experiments, deionized water was attained through the Millipore (18.2 MΩcm) purified water system.

**Preparation of S,B-(CoFe)OOH-H Oxyhydroxides.** The solution combustion synthesis (SCS) was used to prepare the core cobalt oxides through a facile one-step synthesis, followed by an optimized wet chemistry procedure for formulation of the Fe, S, and B amorphous oxyhydroxide shell, as implemented in our recent work.⁶² First, a known amount of Co(NO₃)₂·6H₂O and glycine were dissolved in deionized water. The solution was then placed on a hot plate at 110 °C until near-complete drying of the aqueous phase. The remaining pseudo-aqueous “slug” spontaneously combusts in an autothermal mode. The resultant catalyst powder is then allowed to cool to room temperature in the reaction beaker. The optimized molar ratio of glycine to nitrate salt used was 1:4, which prevented a runaway reaction. The as-prepared catalyst powder is then transferred to a programmable muffle furnace at 800 °C for 5 h for calcination.

In situ deposition of Fe, S, and B was undertaken in a single-step facile wet chemistry method. Briefly, 0.05 g of calcined cobalt oxide from the SCS (herein referred to as C0) was added to 10 mL of deionized water followed by the addition of Fe(NO₃)₂·6H₂O and Na₂S₂O₃·5H₂O. The pH of the solution was then adjusted to 10.5 using 1 M KOH solution. The sample was sonicated with a tip sonicator (Q700 Sonicator) for 30 s and was stirred for another 5 min. CoFe samples that were only S-doped were then removed at this step, vacuum filtered, and left to air-dry overnight in a desicator. S,B-CoFe samples were fabricated with an additional step of adding 50 mL of deionized water followed by an ×10 weight amount ratio of NaBH₄ to cobalt oxide—namely, 0.5 g of NaBH₄. The mixture was sonicated for another 60 s and left static in the beaker for 18 h to ensure complete NaBH₄ reduction and boronation uptake. To collect the S,B-(CoFe)OOH oxyhydroxide samples, vacuum filtration was performed, followed by air-drying overnight in a desicator. The Co/Fe ratio refers to cobalt oxide prepared from SCS and Fe added through the metal nitrate precursor during synthesis. Details of the different ratios of Co/Fe and Fe/S₂ are presented in Table S1 of the array of samples electrochemically screened. The sample fabricated with a high Co/Fe ratio of 29:1 is denoted as S,B-(CoFe)OOH-H, while the sample fabricated with a low Co/Fe ratio of 14:1 is referred to as S,B-(CoFe)OOH-L. The former sample was synthesized with a Fe/S₂ ratio of 14:1 to match the S-doping ratio of the unboronated S-(CoFe)OOH sample. S,B-(CoFe)OOH-L was synthesized with a higher Fe/S₂ ratio of 7:2 to allow for a well-rounded dopant effect comparison on performance differences between catalysts. Scheme 1 summarizes the synthesis steps for both S- and S,B-codoped binary oxyhydroxides, which is similar to our recent work on ternary oxyhydroxides.

**Materials Characterization.** A Kratos AXIS Ultra DLD X-ray Photoelectron Spectroscopy (XPS; Kratos Analytical Ltd., a Shimadzu Group Company, Manchester, United Kingdom) was applied to collect large area survey and high-resolution X-ray photoelectron spectra of S- and S,B-codoped CoFe oxyhydroxide powder samples. A monochromatic Al (Kα) radiation (1486.6 eV) source was operated at 10 kV and 10 mA emission current. The XPS survey spectra were collected using a hybrid magnetic and electrostatic electron lens with 160 eV pass energy and a step size of 1 eV. The high-resolution spectra of Co 2p, Ir 2p, S 2p, O 1s, and B 1s peaks were collected with a pass energy of 20 eV and a step size of 0.1 eV. Both calibration and preliminary fittings of the XPS spectra were undertaken using the implemented Kratos Vision data processing module. Standard calibration using adventitious C 1s (284.6 eV) was employed. High-resolution XPS elemental spectra were then exported, the background was subtracted under the iterated Shirley method, and raw spectra deconvoluted as presented in the manuscript using the integrated Gaussian functions on OriginLab Pro 2020. Details regarding line shape and width attained are tabulated in Tables S2–S6. Deconvoluted Co 2p showing both raw and subtracted background data is presented in Figure S11. This was done for both high (>700 eV) and low (<700 eV) binding energy high-resolution scans. Textural characterization of the as-prepared oxyhydroxides was undertaken through HR-SEM imaging, whereby an FEI Quanta 400 environmental scanning electron microscope (FEI, Oregon) was used. The SEM was operated at a high vacuum mode with 30 kV acceleration voltage and a working distance of around 6.5 mm. The high-resolution transmission electron microscope (HRTEM) images were taken using an FEI Talos F200 TEM. Raman spectroscopy was performed at an excitation wavelength of 532 nm at a focused scan range of 40–1250 cm⁻¹. The crystallinity of SCS prepared cobalt oxide materials was analyzed for comparison using powder XRD spectra collected via a Rigaku Ultima IV Multipurpose X-ray diffractometer (Rigaku Corp., Tokyo, Japan) equipped with cross-beam optics, a fixed monochromator, and a scintillation counter. The XRD radiation source Cu Kα; wavelength of 1.540 Å) was operated at a 40 kV tube voltage and a 30 mA tube current. The XRD spectra were collected in focused beam geometry (Bragg-Brentano geometry, 285 mm goniometer) on the powder catalyst. A 2/3° divergence slit, 10 mm divergence height slit, 1.17 mm scattering slit, and 0.3 mm receiving slit were used. The XRD data were collected using a continuous scan mode in the 2θ range of 5–80° with a step width of 0.02 and a scan speed of 1°/min, then analyzed using integrated Rigaku PDF2x data analysis software with the ICDD PDF4+-2020 library. The resultant peaks were displayed using OriginLab Pro 2020. For quantification of CER species (HClO and ClO⁻), the N,N-
diethyl-p-phenylenediamine (DPD) method using the Hack kit was used. Electrolyte samples were collected after 6 h of chronoamperometry (CA) testing conducted at pH 7 using the phosphate-buffered saline electrolyte at 1.7 V (vs RHE) and analyzed for CER species. Faradaic efficiency (FE) calculations for OER selectivity were performed through gas chromatography (GC) measurements of oxygen evolution at known time intervals during chronoamperometric testing in a gas-tight three-electrode cell. At a given sample time, the currentJA was recorded to initially calculate the theoretical moles of oxygen \( \left( n_{O_2,\text{theory}} = I/zF \right) \) where \( z = 4 \) represents the electrons transferred per ion and \( F = 96485.2 \text{ s A}^{-1} \text{ mol}^{-1} \) represents the Faradaic constant. At a known volumetric flow rate \( (V_{He} \text{ (m}^3/\text{s}) \) of the carrier gas, helium, in this case, the moles of helium are calculated through the ideal gas law \( \left( n_{He} = V_{He}P/RT \right) \) where \( P = 101325 \text{ Pa} \) represents pressure, \( R = 8.314 \text{ kg m}^{-2} \text{s}^{-2} \text{ mol}^{-1} \text{ K}^{-1} \) is the ideal gas constant, and \( T = 293 \text{ K} \) is the temperature. The theoretical oxygen concentration is then calculated as \( C_{O_2,\text{theory}} = n_{O_2,\text{theory}}/\left( n_{He} + n_{O_2,\text{theory}} \right) \). Finally, the FE (%) is calculated by dividing the GC-recorded \( O_2 \) concentration by \( C_{O_2,\text{theory}} \). GC calibration was performed by measuring the known oxygen concentrations (i.e., 1, 2, and 4%) in helium balance) with three datapoints per concentration to obtain a linear calibration curve.

**Electrode Preparation.** For all electrochemical measurements, the electrocatalyst powder samples were deposited on glassy carbon electrodes (GCE; 0.072 cm², Gamry). A homogenous slurry was prepared for each sample by adding 1 mg of the catalyst powder to a 0.54 mL ink solution (100 μL IPA, 400 μL deionized water, and 40 μL of Naion). The solution was stored in 2 mL plastic vials, which were placed in a water bath for 30 s of tip sonication. The slurry was then drop-cast on a polished GCE surface. The slurry was dried at 40 °C for 30 min atop the GCE, yielding a catalyst loading of 0.27 mg/cm².

**Electrochemical Characterization.** All electrochemical experiments were conducted using an electrochemical workstation (Gamry Reference 3000). Electrochemical measurements for alkaline and saline-alkaline electrolysis were performed in a customized electrochemical cell dominated by a three-electrode configuration comprising a glassy carbon (GCE) as the working electrode, Ag/AgCl as the reference electrode at pH 12–14, Hg/Hg₂Cl₂ as the reference electrode at pH 7–12, and a Pt wire as the counter electrode. Parametric tests were conducted on different electrolytes for different conditions of solution pH, salinity, and conductivity; see Table S7. For the duration of testing, the electrolyte was continuously stirred to avoid the accumulation of bubbles at the exposed catalytic surface of the GCE. Prior to linear sweep voltammetry (LSV) tests, cyclic voltammetry (CV) scans (~10 cycles) were performed at a scan rate of 100 mV/s in the same anodic potential range of LSV tests to ensure stabilization of current. The anodic LSV curves were performed in the potential window corresponding to the electrolytic pH value examined at a scan rate of 10 mV/s. To ensure exclusion of oxidation peak effects on the catalytic current densities during overpotential determination, the polarization curves were recorded from the positive to negative potential direction. The below equation was used to ascertain the required potential window with respect to the electrolyte’s pH value:

\[ E = \text{vs RHE} = E_{\text{vs. Ref}} + 0.059pH + E_{\text{Ref}}^0 \]

where “Ref” was Ag/AgCl \( (E_{\text{ref}} = 0.197 \text{ V}) \) for operation from pH 12–14 and Hg/Hg₂Cl₂ \( (E_{\text{ref}} = 0.241 \text{ V}) \) for operation from pH 7–12. Uncompensated resistances \( R_{\text{i}} \) were determined using electrochemical impedance spectroscopy (EIS), and the resultant \( R_{\text{i}} \) were transferred to use in obtaining 90% iR corrections on LSV polarization curves. For impedance spectroscopy, Nyquist plots were obtained in the frequency range of 1 MHz to 1 Hz by passing an input sinusoidal wave of amplitude 5 mV at a potential of 20 mV greater than the overpotential required to achieve a current density of 10 mA cm⁻² to limit bubble film resistances. The realized Nyquist plots were fitted with an appropriate circuit to obtain the charge transfer resistance \( R_{\text{ct}} \) for each catalyst. The electrochemical surface area (ECSA) was approximated through the double-layer capacitance \( (C_{dl}) \) values obtained from the nonohmic potential range, in which the Faradaic reaction cannot be observed, at increased CV scan rates from 20 to 140 mV/s. The ECSA is proportional to \( C_{dl} \) based on the equation \( \text{ECSA} = C_{dl}/C_w \) whereby \( C_w \) in the alkaline electrolyte is approximately a constant \( (0.04 \text{ mF cm}^{-2}) \).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06968.

Particle size distribution; FESEM images; HRTEM images of S- and S,B-codoped oxyhydroxides; HAADF-STEM images of S-(CoFe)OOH; FESEM images, elemental mapping and EDS spectra and quantitative table for the as-prepared S,B-(CoFe)OOH-H oxyhydroxide; current density vs scan rate for oxyhydroxide; polarization curves for S-doped and S,B-(CoFe)OOH-H oxyhydroxides in different pH environments; FESEM images of S,B-(CoFe)OOH-H after CV cycling in different electrolytes; contact angle measurements; polarization curves before and after CV cycling for electro-activating S,B-(CoFe)OOH-H; high-resolution Co 2p XPS deconvolution for S-(CoFe)OOH with and without background Iterated Shirley subtraction; table of dopant ratios for screened and discussed oxyhydroxides; table of high-resolution XPS fitting parameters used in deconvolution; table of electrolytes used for electrochemical testing; \( R_{\text{i}} \) values from Nyquist plots under different electrolytes; tabulated overpotentials at 300 mA cm⁻² of S-(CoFe)OOH and S,B-(CoFe)OOH-H under different electrolytes tested (PDF).

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Notes

The authors declare no competing financial interest. The raw and processed data required to reproduce these findings are available upon request from the corresponding author.

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