

RESEARCH ARTICLE OPEN ACCESS

Selective Electrolysis of Water Under Artificial Seawater Conditions Using Transition Metal Borate Anodes

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Received: 19 December 2025 | **Revised:** 1 March 2026 | **Accepted:** 2 March 2026

Keywords: CER | DFT | OER | hydroxide precipitation | seawater electrolysis

ABSTRACT

Direct seawater electrolysis overcomes one major hurdle in sustainable hydrogen production, viz. the requirement to use high-purity water, which is currently a scarce resource for ~80% of the global population. On the other hand, the natural composition of seawater makes it unsuitable for direct use in conventional electrolyzer systems, primarily due to the occurrence of the chlorine evolution reaction (CER) at the anode, instead of the desired oxygen evolution reaction (OER), and the build-up of insulating $\text{Mg}^{2+}/\text{Ca}^{2+}$ hydroxides at the cathode. Herein, we present an electrolyzer fed with artificial seawater with no added electrolyte and enabling selective splitting of H_2O , rather than H_2 generation coupled to the CER. This selectivity was provided by the anodes derived from a cobalt iron boride material, which was predicted to favor the OER rather than the CER by the density functional theory calculations. The compact design of the electrode-separator assembly suppressed the cathodic $\text{Mg}/\text{Ca}(\text{OH})_2$ precipitation. Robust operation of the electrolyzer over one week was demonstrated at 100 mA cm^{-2} with a cell voltage of ca. -2.6 V at $80 \pm 1^\circ\text{C}$. These operating conditions were selected based on a preliminary techno-economic analysis as a realistic benchmark for cost-competitive hydrogen production.

1 | Introduction

Coastal arid regions and offshore sites worldwide offer abundant solar, wind, and wave energy, making them ideal locations for generating renewable electricity that can be transformed into hydrogen and other green fuels for storage or distribution [1, 2]. Arid zones such as the Middle East, South Africa, western North America, Australia, and western China offer high solar irradiance [1, 3], while coastal areas of northern Europe, southern Alaska, the southern tip of South America, Greenland, Australia, and Asia are highly favorable for wind energy generation [4]. A key resource missing in most of these areas is high-purity

water, which is limited in its availability to over 80% of the global population [5, 6] but is required for stable operation of the state-of-the-art electrolyzers [7, 8].

On a positive side, technoeconomic studies suggest that seawater desalination would contribute a small fraction to the overall CapEx and energy consumption of a water electrolysis plant [9], though this share will rise as the cell stack costs decline [10]. Moreover, when expressed in absolute values, the CapEx and OpEx of desalination are not insignificant. Specifically, construction of a desalination plant supplying water for a 1 GW H_2 production facility would currently cost ca. \$10–20 million,

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with annual OpEx reaching up to one-third of the CapEx [11]. These costs are further exacerbated by the intermittent operation of renewable-powered electrolysis plants, which intensifies maintenance frequency and increases the likelihood of downtime in the hydrogen output [12]. Moreover, offshore energy plants that have direct access to solar, wind, and tidal resources are constrained by limited space and strict weight limits, making compact systems essential [13]. In addition, remote maintenance of separate desalination units increases system OpEx, while marine-based hydrogen generation units crucial for military and rescue services require robust energy systems capable of using seawater and brackish water while maintaining high mobility. To capitalize on these energy resources without relying on additional water purification infrastructure, direct electrolysis of seawater, which accounts for about 97% of Earth's surface water and is readily available in arid locations [14, 15], is actively explored.

During direct seawater electrolysis, the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode are hindered by the complex ionic composition of seawater, particularly by the presence of Cl^- , Mg^{2+} , and Ca^{2+} [16]. At the anode, the chlorine evolution reaction (CER) is in direct competition with the OER. Although Cl_2 is a commercially valuable product, the quantity of chlorine gas generated along with hydrogen by an HER/CER process would rapidly exceed the current global demand (~ 88 million tonnes of Cl_2 per annum) [17]. Additionally, Cl_2 is highly corrosive, and suppressing the CER would avoid the need for specialised corrosion-resistant components and reduce maintenance requirements. While the CER is thermodynamically less favourable than the OER, with a maximum difference in standard electrode potential of 0.48 V at $\text{pH} \geq 8.4$ under standard conditions [6, 15], chloride oxidation is kinetically preferred with conventional OER anodes based on Ir, Ru, and third-row transition metal oxides [18]. At the cathode, the local pH gradient resulting from the HER causes OH^- accumulation, which reacts with Mg^{2+} and Ca^{2+} to form insoluble, electrically insulating hydroxides of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ [19]. These non-conductive layers impede the HER and significantly shorten the cell lifespan, requiring frequent maintenance.

To address these challenges, various strategies have been proposed. These include innovations in the electrolyzer architecture [20–22], electrode materials [23–25], introduction of buffer electrolytes [26, 27], and seawater alkalization prior to electrolysis [28, 29]. The pre-alkalization approach attracts particular attention as it eliminates both major problems by precipitating $\text{Mg}/\text{Ca}(\text{OH})_2$ before introducing seawater into the electrolyzer and providing pH conditions that are thermodynamically favorable (by ~ 0.48 V) for the OER as compared to the CER [15]. The promise of this approach was recently demonstrated using an anion exchange membrane (AEM) electrolyzer equipped with a Ni_xS_y -based anode fed with alkalized (1 M KOH) seawater and an N_2 -fed Ni_xP_y -based cathode [22]. Operation of this device at 400 mA cm^{-2} and 98% OER faradaic efficiency (FE) required an initial cell voltage of -1.8 V at 60°C , and it degraded at an average rate of 5300 $\mu\text{V h}^{-1}$ over 100 h. The key limitation of this strategy is the irreversible consumption of KOH during the precipitation of $\text{Mg}^{2+}/\text{Ca}^{2+}$ as well as the AEM degradation at high OH^- con-

centration, required for effective operation [30]. An alternative approach is to utilize bipolar membranes (BPM) on the anode and a cation exchange membrane (CEM) on the cathode, with seawater supplied to the electrolyzer via capillary action from a reservoir positioned directly below the cell [31]. The BPM-affixed anode excluded Cl^- ions via Donnan exclusion to avoid the CER, while the CEM-affixed cathode rejected $\text{Mg}^{2+}/\text{Ca}^{2+}$ through ion sieving effects to prevent hydroxide precipitation. Using a Pt-coated Ti mesh anode and an IrO_2 -coated Ti mesh cathode, such a device was reported to sustain $\sim 100\%$ OER and HER faradaic efficiency at 100 mA cm^{-2} and -3.1 V for 12 h at ambient temperature.

In a most cost-effective scenario, direct seawater electrolyzers would not use high-cost [32] ion-selective membranes that are inevitably poisoned by the seawater ions but would have an architecture similar to that of the traditional alkaline water electrolyzers. An elegant strategy to exclude parasitic seawater ions without consuming KOH and avoiding the use of the ion-selective solid electrolytes was proposed by Xie et al., [20]. This study introduced hydrophobic porous polytetrafluoroethylene (PTFE) membranes protecting an electrolytic cell containing a Mo- Ni_3S_2 -functionalised Ni foam anode and a PtNi mesh cathode separated by a high-concentration KOH electrolyte. The PTFE permitted water vapor uptake into the electrolytes while suppressing the Cl^- and $\text{Ca}^{2+}/\text{Mg}^{2+}$ permeation, allowing essentially unhindered conventional alkaline water electrolysis to occur at 250 mA cm^{-2} and -1.9 V for ~ 3200 h at ambient temperature. Arguably, this report presents one of the most significant recent developments in the seawater electrolysis field.

Parallel to the innovations at the device level briefly surveyed above, a significant stream of research focuses on the development of electrocatalysts that can selectively promote the OER in saline water and/or seawater in the presence of the naturally occurring species. The most convincing studies of this kind directly quantified the electrochemically generated chlorine products in the electrolyte solutions to demonstrate significant (for example, for $\text{SiO}_x/\text{RuO}_x$ with $FE_{\text{CER}} \approx 0.4\%$ at 2 mA cm^{-2} in 0.6 M NaCl [33]), or partial (e.g. for CoFe-PB with $FE_{\text{CER}} \approx 20\%$ at 0.8 mA cm^{-2} in seawater electrolyte [34], and $\text{Pb}_2\text{Ru}_2\text{O}_{7-x}$ with $FE_{\text{CER}} \approx 32\%$ at 50 mA cm^{-2} in filtered seawater [35]) suppression of the CER. However, many other reports in this area do not provide adequate or any data on the quantification of free chlorine. Other limitations of the existing work include operation at low current densities (< 100 mA cm^{-2}), use of model three-electrode rather than electrolyzer conditions, no quantification of the solid hydroxides accumulated at the cathode, and the lack of durability assessment with the performance reported over short periods of operation only (< 1 day).

Our present work aimed to develop selective anodes for the seawater electrolysis and integrate them into an electrolyzer fed with an electrolyte solution with a composition representing that of seawater that avoids the pitfalls above. We present a device equipped with a Zirfon UTP 220 separator along with a cobalt-based anode and cathode that sustains H_2O splitting into O_2 and H_2 when fed with artificial seawater with no additional electrolyte added.

2 | Results and Discussion

While various materials have been proposed to selectively catalyze the OER in non-buffered solutions containing seawater-level concentrations of Cl^- , our attempts to reproduce some of the most prominent reports were not successful. Most catalysts often lacked the OER selectivity and were prone to corrosion when exposed to chloride-containing electrolyte solutions. Hence, we focused our attention on underexplored catalysts derived from transition metal borides. Such materials have been previously investigated for the alkaline water [36, 37] and alkalinized seawater oxidation [38, 39], but not for the direct seawater electrolysis. Metal borides are inherently unstable during the OER and can be expected to undergo surface reconstruction, transforming into borates upon electrooxidation, similar to other non-oxide materials used for the OER [40–43]. Rather than being a drawback, this instability promotes the in situ formation of stable oxyanion species that serve as catalytic OER-selective sites under such operating conditions. Hence, we assessed the theoretical possibility of the cobalt and iron-cobalt borates, as representative examples of the materials of interest therein, to preferably catalyze the OER rather than the CER using density functional theory (DFT) calculations (Figure 1).

For $\text{CoBO}_3(100)$, equivalent to (010), the surface exhibits four-coordinated Co (4c-Co) and two-coordinated B (2c-B) exposed atoms with vacancies available for the adsorption of the OER and CER intermediates (left-hand side image in Figure 1a). To model a bimetallic cobalt-iron system, one of the Co atoms on the $\text{CoBO}_3(100)$ surface was replaced by Fe. This modification alters the surface landscape, generating structural anisotropy that necessitates modelling the $\ast\text{Cl}$ and $\ast\text{OH}$ adsorbates at specific binding sites on the surface shown in the left-hand side image in Figure 1b. Calculations at the revised Perdew-Burke-Ernzerhof (RPBE) level of theory in an aqueous solution show that the surface B atoms are preferred binding sites for both $\ast\text{Cl}$ and $\ast\text{OH}$, as they produce more energetically favorable intermediates compared to adsorption via both Co and Fe atoms (right-hand side images in Figure 1).

Assuming that these B-based anchor points on the surface are competitive sites for both CER and OER, the differences in the relative free energies of their corresponding first steps ($\Delta_{\text{R}}G$), viz. $\ast + \text{Cl}^- \rightarrow \ast\text{Cl} + \text{e}^-$ and $\ast + \text{H}_2\text{O} \rightarrow \ast\text{OH} + \text{H}^+ + \text{e}^-$ ($\ast$ is the adsorption site), define the selectivity between the two processes. In other words, if the active site preferentially adsorbs $\ast\text{Cl}$, it becomes unavailable for the adsorption of $\ast\text{OH}$ and hence incapable of catalyzing the OER. In the case of CoBO_3 , $\Delta_{\text{R}}G$ for both $\ast\text{OH}$ and $\ast\text{Cl}$ formation is positive, but the latter is approximately 0.04 eV more energetically preferable. This difference can be converted into the OER : CER selectivity of 85: 15 (1 atm, 25°C , $[\text{Cl}^-] = 0.6 \text{ M}$, $\text{pH} = 7$), under a simplified assumption that the rates of the two reactions are related as $\exp(-\frac{\Delta_{\text{R}}G^{\text{OER}} - \Delta_{\text{R}}G^{\text{CER}}}{RT})$. Notwithstanding the adsorption of the CER and OER intermediates is predicted to occur on the B sites, the introduction of Fe into cobalt borate notably stabilizes the $\ast\text{Cl}$ and $\ast\text{OH}$ adsorbates, whose energies of adsorption now become 0.19 eV and -0.13 eV, respectively (right-hand side images in Figure 1b). Most importantly, this modification also enhances the difference in the $\Delta_{\text{R}}G$ for the OER and CER up to 0.31 eV, suggesting that the OER: CER selectivity ratio can be as high

as 100:0 for this system, based on the same assumption as above.

We have also analyzed the CER vs. OER competition for the boron-free systems following the same methodology as above. The resulting differences in the $\Delta_{\text{R}}G$ for the competing steps of the reactions indicated a strong preference of the CER over the OER for both CoOOH and Co_3FeOOH controls under conditions relevant herein (Figure S4).

To validate the theoretical predictions, we synthesized a series of boride-containing materials, $\text{M}[\text{B}]_x[\text{OH}]_y$, by reacting transition metal salts with NaBH_4 under basic aqueous conditions ($\text{pH} 13$). In this process, NaBH_4 served as both a reducing agent and a boron source. Electrochemical experiments were undertaken first in unbuffered 0.6 M NaCl to define the best-performing catalysts and then in artificial seawater in an electrolysis cell that mitigates hydroxide precipitation at the cathode [44]. The CER vs. OER selectivity was determined in all relevant experiments through the conventional spectrophotometric DPD (*N,N*-diethyl-*p*-phenylenediamine) analysis of free chlorine (Figure S1), which was dominated by dissolved HOCl/OCl^- under conditions employed herein. Indeed, only H_2 and O_2 gasses, along with traces of N_2 , were detected by gas chromatographic analysis during the electrolyzer tests at elevated temperature and current densities, as discussed in the final section of the manuscript (vide infra). Formation of the higher-oxidation-state chlorine species, like ClO_3^- , would be only possible through secondary chemical reactions in the solution like disproportionation of HOCl/ClO^- , which are irrelevantly slow under conditions employed in our work [45].

2.1 | Electrooxidative Activity of the Boride-Derived Catalysts in 0.6 M NaCl

The electrooxidative activity of the catalysts derived from borides of cobalt, nickel, manganese, and iron was first assessed by cyclic voltammetry and short-term chronopotentiometry in 0.6 M NaCl at ambient temperature ($23 \pm 2^\circ\text{C}$) (Figure 2a; Figure S6a, and Table S3). Among the materials tested, the highest electrooxidation rates were provided by the cobalt-based catalysts, and especially those derived from bimetallic $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$, which demonstrated measurable activity at potentials less positive than 2.0 V vs. reversible hydrogen electrode (RHE) (Figure 2b). In contrast, electrodes functionalized with $\text{Mn}[\text{B}]_x[\text{OH}]_y$, $\text{Ni}[\text{B}]_x[\text{OH}]_y$, and $\text{Fe}[\text{B}]_x[\text{OH}]_y$ produced measurable oxidative currents at potentials more positive than 2.1 V vs. RHE (Figure S6b). Quasi-steady-state polarization plots derived from the short-term chronopotentiometric data (i_{R}^{u} -corrected; R_{u} is uncompensated resistance derived from the electrochemical impedance spectroscopy) demonstrated acceptable linearity up to 20 mA cm^{-2} for all materials except for $\text{Co}[\text{B}]_x[\text{OH}]_y$, where deviation from the theoretically predicted behavior was seen at $j > 4 \text{ mA cm}^{-2}$ (Figure 2c; Figure S6c, and Table S3). This is likely due to degradation of $\text{Co}[\text{B}]_x[\text{OH}]_y$, which was evident from the progressively increasing potential even during the short-term galvanostatic test at 20 mA cm^{-2} (Figure 2b). In contrast, voltammetric curves and chronopotentiograms for other examined B-containing materials did not show signs of degradation, providing an initial indication of the stability of the boride-derived catalysts during

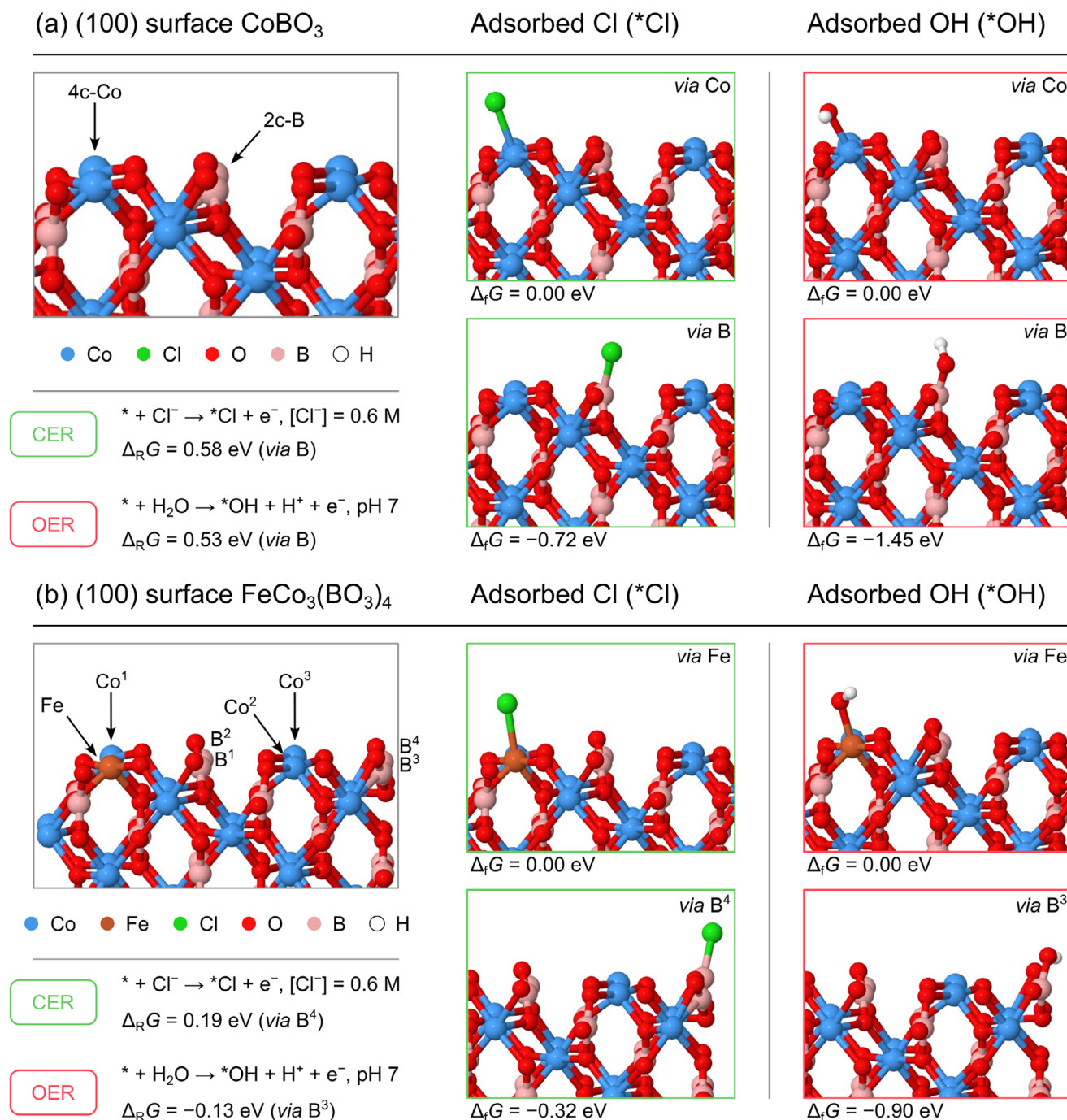


FIGURE 1 | DFT analysis of the CER and OER on the cobalt borate and cobalt-iron borate surfaces. Optimized structures of the (a) CoBO_3 and (b) $\text{FeCo}_3(\text{BO}_3)_4$ (100) surfaces, along with the most stable *Cl and *OH configurations calculated at the RPBE level of theory in water, along with corresponding free energies of formation ($\Delta_{\text{f}} G$). $\Delta_{\text{R}} G$ are relative free energies for the first steps of the CER and the OER, i.e. chloride oxidation into *Cl at $[\text{Cl}^-] = 0.6 \text{ M}$ and H_2O oxidation into *OH at pH 7. Color code: Co (blue), Fe (brown), Cl (green), O (red), B (pink), and H (white). Extended data are provided in Figures S3 and S5.

electrooxidation of 0.6 M NaCl aqueous solutions. As a boron-free control, we tested a $\text{Co}_3\text{Fe}_1\text{O}_n\text{H}_m$ material, which showed lower electrooxidation activity as compared to $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ and even $\text{Co}[\text{B}]_x[\text{OH}]_y$ (Figure 2a and Table S3). This result suggests that the presence of boron-based species promote the electrooxidation activity of the cobalt-based anodes in the chloride-containing electrolyte solution.

It was also useful to compare the performance of the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -modified electrodes to that of the dimensionally stable anode, viz. mixed Ir and Ru oxides on a Ti mesh support (DSA), which is one of the most robust anode materials designed for operation in saline water [46]. While DSA exhibited expectedly higher activity, it was better than that of the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -modified electrodes by not more than 0.05 V within the current

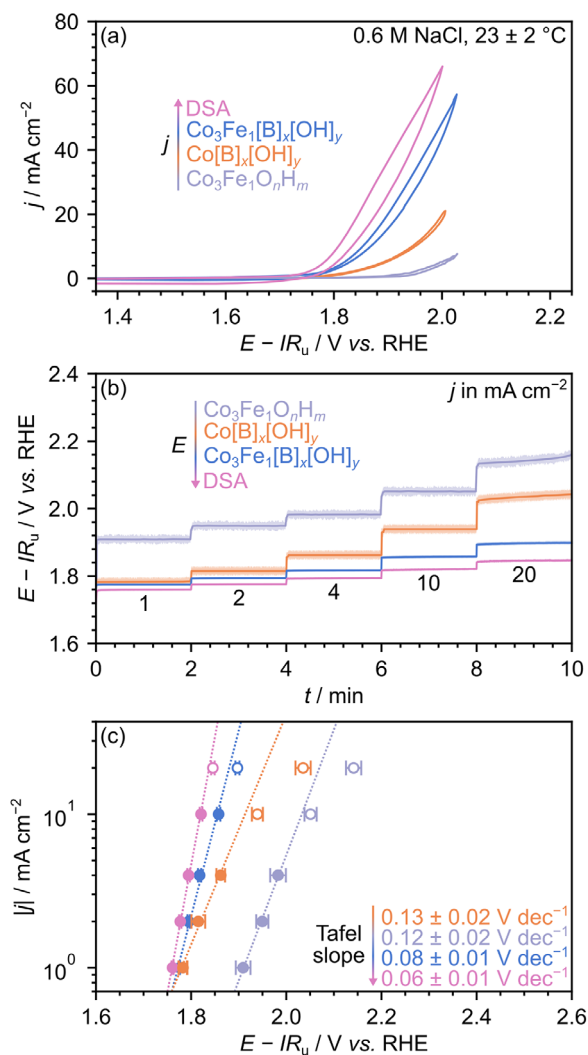


FIGURE 2 | Initial electrooxidative activity of the cobalt-based anodes and DSA in 0.6 M NaCl. (a) Stabilized cyclic voltammograms (scan rate, $\nu = 0.010 \text{ V s}^{-1}$; third scans), (b) chronopotentiograms at current densities shown in the plot, and (c) the OER + CER polarization plots derived from the data in panel b (symbols are experimental data; lines are linear fits within ranges of observed linearity (●)), the inverse slopes of which represent Tafel slopes shown in the figure) for $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ (blue), $\text{Co}[\text{B}]_x[\text{OH}]_y$ (orange), $\text{Co}_3\text{Fe}_1\text{O}_n\text{H}_m$ (lavender), and DSA (pink). Data in panels b–c are shown as mean (lines, symbols) $\pm$ standard deviation (shading, error bars) derived from testing $n = 3$ independent samples of each type. Borides were deposited onto a glassy carbon rotating disk electrode (0.2 cm^2) at 0.25 mg cm^{-2} . DSA was a free-standing mesh with a geometric surface area of 1 cm^2 . Currents are normalized to the geometric surface area of the electrodes; potentials were manually IR_u -corrected post-measurements. Experiments were undertaken at $23 \pm 2^\circ\text{C}$ and a glassy carbon electrode rotation rate of 1600 rpm or under stirring at 1600 rpm by a Teflon-lined bar for DSA.

density range shown in Figure 2b. At the same time, the Tafel slope derived from the $\log |j|$ vs. E steady-state data was lower for the DSA ($0.06 \pm 0.01 \text{ V dec}^{-1}$) as compared to $0.08 \pm 0.01 \text{ V dec}^{-1}$ measured with $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ (Figure 2c).

It is important to recognize that the anodic currents recorded in the Cl^- -containing solutions present a combination of the

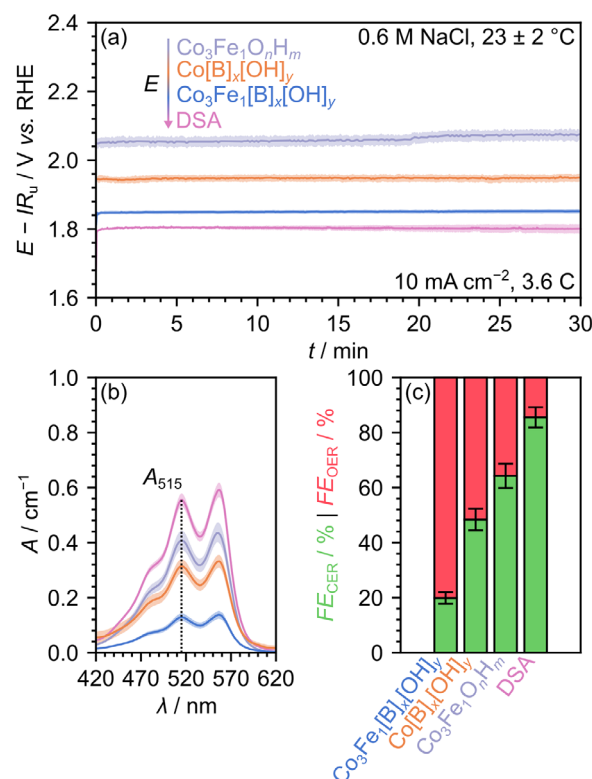


FIGURE 3 | The CER vs. OER selectivity for the cobalt-based anodes and DSA in 0.6 M NaCl. (a) IR_u -corrected chronopotentiograms at 10 mA cm^{-2} (per geometric surface area of the electrodes), (b) spectrophotometric DPD analysis of free chlorine in the electrolyzed solutions after experiments in panel a, and (c) corresponding faradaic efficiencies of the CER (green) and OER (red) for $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ (blue), $\text{Co}[\text{B}]_x[\text{OH}]_y$ (orange), $\text{Co}_3\text{Fe}_1\text{O}_n\text{H}_m$ (lavender), and DSA (pink). Data are shown as mean (curves, bars) $\pm$ standard deviation (shading, error bars) derived from testing $n = 3$ independent samples of each type.

OER and CER occurring in parallel [46]. The preference of the investigated materials to catalyze either of these reactions in 0.6 M NaCl was investigated at 10 mA cm^{-2} for the cobalt-based materials and DSA, while less catalytically active materials based on Mn, Ni, and Fe were tested at 5 mA cm^{-2} until a total charge of 3.6 C passed (Figure 3a; Figure S7a, and Table S4).

As expected [47], DSA generated the highest concentration of free chlorine, which was approximately 4.3- and 1.8-fold higher than those found for $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ and $\text{Co}[\text{B}]_x[\text{OH}]_y$, respectively (Figure 3b). Converting these data into faradaic efficiency (FE) values, we found that DSA achieved a FE_{CER} of $86\% \pm 4\%$, consistent with a previous study using similar current density and temperature [48]. Among electrodes functionalized with monometallic borides, the highest CER selectivity of $48\% \pm 4\%$ ($FE_{\text{OER}} = 52\% \pm 4\%$) was found for $\text{Co}[\text{B}]_x[\text{OH}]_y$, while the best result in the given context was provided by $\text{Mn}[\text{B}]_x[\text{OH}]_y$, showing FE_{CER} of only $11\% \pm 1\%$ (Figure S7c). The $\text{Ni}[\text{B}]_x[\text{OH}]_y$ - and $\text{Fe}[\text{B}]_x[\text{OH}]_y$ -modified electrodes provided intermediate FE_{CER} values of $30\% \pm 2\%$ and $27\% \pm 1\%$, respectively. However, it should be recognized that all electrodes based on the non-cobalt borides sustained relatively stable operation at only 5 mA cm^{-2} at potentials as positive as 2.30–2.37 V vs. RHE (Figure S7a), as opposed to 10 mA cm^{-2} at $1.94 \pm 0.01 \text{ V}$ vs. RHE for $\text{Co}[\text{B}]_x[\text{OH}]_y$. The

bimetallic $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ system produced low CER faradaic efficiency of $20\% \pm 2\%$ ($FE_{\text{OER}} = 80\% \pm 2\%$) at 10 mA cm^{-2} and $1.86 \pm 0.01 \text{ V}$ vs. RHE, i.e. significantly outperforming both Co and Fe monometallic catalysts (Figure 3c). The difference in the CER vs. OER selectivity for the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ - and $\text{Co}[\text{B}]_x[\text{OH}]_y$ -derived materials qualitatively followed the trend predicted by the DFT calculations (Figure 1). The $\text{Co}_3\text{Fe}_1\text{O}_n\text{H}_m$ control material demonstrated substantially higher CER selectivity of $64\% \pm 4\%$ as compared to the borate-containing catalysts (Figure 3c), which was again consistent with the DFT predictions (Figure S4). Thus, both theoretical and experimental results point towards the important role of the boron-based species in suppressing the CER during electrooxidation of the chloride-containing electrolyte solutions.

To provide an additional point of comparison, we also synthesized and tested mixed manganese-molybdenum-tungsten, $[\text{Mn-Mo-W}]\text{O}_x$ [49], and manganese-molybdenum-tin oxides, $[\text{Mn-Mo-Sn}]\text{O}_x$ [50], electrodeposited on DSA. Both of these systems were reported as some of the most effective OER-selective catalysts known to date that produce only $\sim 1\%$ FE_{CER} at 100 mA cm^{-2} for over 2500 h of electrooxidation of aqueous 0.5 M NaCl [49, 50]. Upon testing these materials under the same conditions as described above, we found that both trimetallic oxide systems exhibit lower electrooxidative activity than the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -functionalized electrodes, requiring 1.92 ± 0.01 ($[\text{Mn-Mo-W}]\text{O}_x/\text{DSA}$) and $1.88 \pm 0.01 \text{ V}$ vs. RHE ($[\text{Mn-Mo-Sn}]\text{O}_x/\text{DSA}$) to achieve 10 mA cm^{-2} with high Tafel slopes of 0.17 ± 0.01 ($[\text{Mn-Mo-W}]\text{O}_x/\text{DSA}$) and $0.11 \pm 0.02 \text{ V dec}^{-1}$ ($[\text{Mn-Mo-Sn}]\text{O}_x/\text{DSA}$) (Figure S8 and Table S3). The corresponding FE_{CER} were $24\% \pm 2\%$ ($[\text{Mn-Mo-W}]\text{O}_x/\text{DSA}$) and $51\% \pm 6\%$ ($[\text{Mn-Mo-Sn}]\text{O}_x/\text{DSA}$) (Figure S9 and Table S4). These results indicate that the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -derived materials might be more suitable for the selective catalysis of the OER in unbuffered solutions containing NaCl, at least under conditions examined herein. Hence, we further focused our study on the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -based electrodes.

2.2 | Catalytically Active State of the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -Derived Material

Morphologic and compositional analysis was performed using scanning electron microscopy and energy-dispersive spectroscopy mapping (SEM-EDS). The as-synthesized $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ material consisted of aggregated nanoparticles with the size ranging from 10 to 50 nm (Figure S13). According to EDS, all three elements were distributed uniformly throughout the sample with the expected Co: Fe atomic ratio of ca. 3: 1 and an apparent concentration of boron as high as 42 at.% (Table S15). However, quantification of B with EDS is subject to a significant degree of uncertainty due to the low-energy X-ray emission ($< 1 \text{ keV}$) and a partial overlap between the B K_α (0.18 keV) and C K_α signals (0.28 keV) [51]. To address this, as-synthesized $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ was characterized by inductively coupled plasma mass spectrometry (ICP-MS; Figure S2a), again showing a close to 3:1 Co : Fe atomic ratio, but with a much lower boron content of ca. 9.3 at.% (with respect to Co+Fe+B; Table S15).

Morphological and structural features of $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ were further probed by the transmission electron microscopy (TEM)

analysis (Figure S14). TEM revealed that the material contained nanoparticles without well-defined lattice fringes, showing only faint and discontinuous patterns in some regions. This was corroborated by the X-ray diffraction (XRD) analysis of $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ producing essentially featureless patterns, attesting to the amorphous nature of the material (Figure S15). After 30 min of operation at 10 mA cm^{-2} in 0.6 M NaCl , no significant XRD signals were detected as well (Figure S15). TEM analysis suggested that a thin ($< 10 \text{ nm}$) surface layer of the nanoparticles was partially transformed into different species as compared to the bulk of the material, likely due to electrooxidation (Figure 4a; Figure S16).

X-ray absorption near edge structure (XANES) recorded for freshly prepared $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ at the Co K-edge was within error similar to that of $\text{Co}(\text{OH})_2$ (Figure 4b). The Co K-edge extended X-ray absorption fine structure (EXAFS) spectra and their Fourier transforms (FT) were also consistent with $\text{Co}(\text{OH})_2$ (Figure 4c-d). The Fe K-edge XANES spectrum of the as-synthesized material could be fitted by a linear combination of the reference data for $\text{Fe}^{\text{II}}\text{O}$ (ca. 28 at.%) and $\text{NiFe}^{\text{III}}\text{OOH}$ (ca. 72 at.%), indicating the presence of both Fe^{II} and Fe^{III} (Figure S17 and S18). The Fe K-edge EXAFS and FT EXAFS also exhibited features that could be interpreted as a mix of different metal environments (Figure 4c,d). Comparisons of the Co K- and Fe K-edge FT EXAFS revealed similarity in the first coordination sphere environment of the two metals within $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ (Figure 4d). Simulations of the EXAFS confirmed that the first-shell M-O and second-shell M-M distances were consistent between Co and Fe within uncertainty for as-synthesized $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ (Tables S5 and S6 and Figure S18). This suggests similar local coordination environments for Fe and Co within the resolution of the measurement, consistent with the homogeneous distribution of the two metals within the as-synthesized material (Figure S13).

When probed in situ at 2.2 V vs. RHE, the Co K- and Fe K-edge XANES of the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -modified electrodes shifted towards higher energies closer to CoOOH and NiFeOOH , suggesting oxidation of both metals (Figure 4b; Figure S17). Correspondingly, the in situ Co K-edge EXAFS and FT EXAFS were now similar to those of CoOOH (Figure 4c,d). The in situ Fe K-edge EXAFS spectra showed strong attenuation of the second coordination sphere, indicating loss of the longer-range order around Fe under electrooxidative conditions (Figure 4c). This change is consistent with the coexistence of multiple Fe-containing environments, and in situ EXAFS does not uniquely resolve the fate of Fe beyond the observed change in local coordination. The in situ Fe K-edge EXAFS was all dominated by an octahedral Fe site with $6 \times \text{Fe-O}$ atoms, indicating that Co and Fe occupied structurally different sites during electrooxidation, in contrast to the as-synthesized material (Figure 4d). This conclusion was further supported by simulations of the Co K- and Fe K-edge EXAFS data (Tables S7 and S8 and Figure S18).

Survey X-ray photoelectron spectra (XPS) of as-synthesized $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ confirmed the presence of all expected elements on the material surface, viz. both metals, boron, oxygen, and adventitious carbon (Figure S19a). The Co 2p and Fe 2p spectra demonstrated the predominance of the oxidized, likely Co^{2+} and Fe^{3+} , metal states (Figure 4e,f). At the same time, detectable signals of metal borides were also found in both Co 2p and Fe 2p

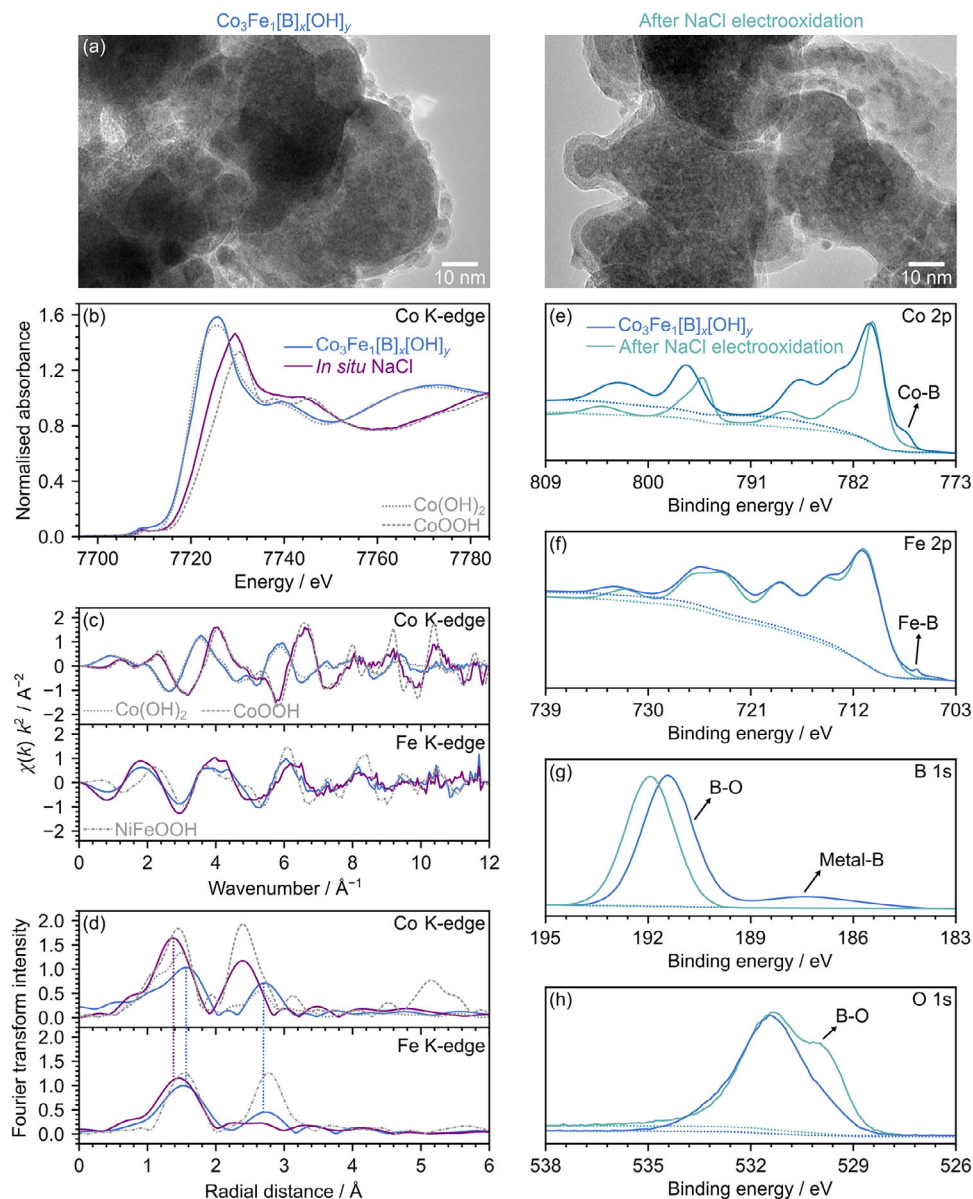


FIGURE 4 | Characterization of $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ before, during, and after oxidation of 0.6 M NaCl. (a) Transmission electron micrographs before (left) and after (right) 30 min of operation at 10 mA cm^{-2} . (b) Co K-edge XANES, (c) Co K- and Fe K-edge EXAFS, (d) Co K- and Fe K-edge FT EXAFS, (e) Co 2p, (f) Fe 2p, (g) B 1s, and (h) O 1s spectra recorded for as-synthesized $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ (blue), in situ at 2.2 V vs. RHE (purple), and after 30 min of operation at 10 mA cm^{-2} (teal). Supplementary data are shown in Figures S17–S19. Panels b–d also show data for $\text{Co}(\text{OH})_2$ (dotted), CoOOH (dashed), and NiFeOOH (dash-dotted). Conditions of the electrochemical experiments were as in Figure 3.

spectra of the as-synthesized material at ca. 777.8 and 706.5 eV, respectively [52], accompanied by a clear boride signal in the B 1s spectrum at ca. 187.3 eV (Figure 4g) [53]. However, the dominant boron state was oxidized [B-O], i.e. borate, giving rise to an intense signal at 191.6 eV [53]. After electrooxidation of 0.6 M NaCl, the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -derived material produced a [B-O] B 1s signal shifted towards higher binding energies as compared to the as-prepared material, which indicated further oxidation of boron [36]. This was accompanied by the evolution of an additional O 1s signal at 531.2 eV, which might be associated with the [B-O] species (Figure 4h) [54]. Electrochemical treatment eliminated all indications of the presence of borides on the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ surface, and the atomic [Co+Fe]:B ratio slightly decreased from ca. 92:8 to 94:6.

Overall, the aggregate of the physical characterization data indicated that the as-synthesized $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ material consisted of a mixed phase of cobalt-iron hydroxide, borate, and boride. Upon electrooxidation, the boride component was lost, yielding predominantly (oxy)hydroxide and borate species. The high OER selectivity of $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ can be attributed primarily to the surface borate species detected by XPS and predicted by DFT to suppress the CER kinetics (Figure 1). However, it should be noted that $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$, initially containing Fe substitutionally incorporated within the cobalt-based hydroxide/borate structure, underwent electrochemically induced restructuring resulting in the formation of a disordered or isolated octahedral Fe state, which was now structurally different to that of Co (Figure 4d). This might be one of the reasons for the remaining CER activity

of the $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ -modified electrodes in the experimental studies, since the best OER selectivity was predicted by DFT for a material where Fe is substitutionally doped into the Co borate structure (Figure 1). Besides, while DFT predicted relatively high OER overpotentials for the cobalt-based borate materials (Figure S5), the experiments demonstrated their satisfactory performance (Figure 2). In this context, one should keep in mind the inevitable differences between the close-to-ideal theoretical structures used for modelling and more complicated, less structurally ordered real catalytic materials. Hence, we can conclude on the qualitative agreement between the experiment and DFT results but refrain from establishing any quantitative correlations.

2.3 | Seawater Electrolysis and Techno-economic Analysis

Next, we aimed to translate the model results obtained with 0.6 M NaCl in a three-electrode cell into an electrolyzer cell prototype operating under more practically relevant conditions. Apart from an OER-selective anode, such electrolyzer would also require a robust cathode capable of efficient operation in unbuffered near-neutral solutions. Among different possibilities, we examined Co_1Mo_1 and Ni_1Mo_1 , which were previously benchmarked as high-activity HER catalysts for both alkaline and neutral conditions [55]. The catalysts were electrodeposited onto a Mo mesh, producing a uniform coating of particles with the size ranging from 200 to 400 nm (Figure S20).

When probed by cyclic voltammetry in 0.6 M NaCl at $23 \pm 2^\circ\text{C}$, the Mo mesh electrode functionalized with Co_1Mo_1 or Ni_1Mo_1 exhibited significantly higher HER activity compared to the unmodified Mo mesh (Figure 5a; Table S9). Among these, $\text{Co}_1\text{Mo}_1/\text{Mo}$ demonstrated the best performance, though it was still outperformed by a Pt mesh benchmark under the potentiodynamic conditions within the potential range examined (Figure 5a). Short-term chronopotentiometric results at current densities down to -40 mA cm^{-2} also showed lower activity of the $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh against Pt mesh, but operation at more practically relevant -100 and -200 mA cm^{-2} alleviated this difference (Figure 5b,c). Specifically, the $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh electrode achieved a current density of -100 mA cm^{-2} at an overpotential of $0.65 \pm 0.01 \text{ V}$, which was close to $0.59 \pm 0.01 \text{ V}$ for the Pt mesh (Figure 5b,c). While the HER Tafel slope for the $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh was comparable to that of the Pt mesh, the $\log |j|$ vs. E dependence for the latter lost linearity at current densities above -40 mA cm^{-2} (Figure 5c). As a result, the $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh outperformed the Pt mesh at -200 mA cm^{-2} (Figure 5c; Table S9). This deterioration in the performance of the platinum electrode might be associated with cathodic corrosion of the noble metal [56], which can be additionally facilitated by the presence of Cl^- inducing formation of platinum-chloro complexes [57]. However, deeper investigation of this phenomenon goes beyond the focus of the present work.

With both anode and cathode materials identified, we then proceeded to their integration into an electrolysis cell. Previously, we demonstrated that a zero-gap cell configuration mitigates accumulation of insoluble hydroxides at the cathode during the artificial seawater electrolysis by reducing local pH gradients [44]. Herein, a further upgraded version of this cell was employed, with a Zirfon UTP 220 separator compressed between the anode

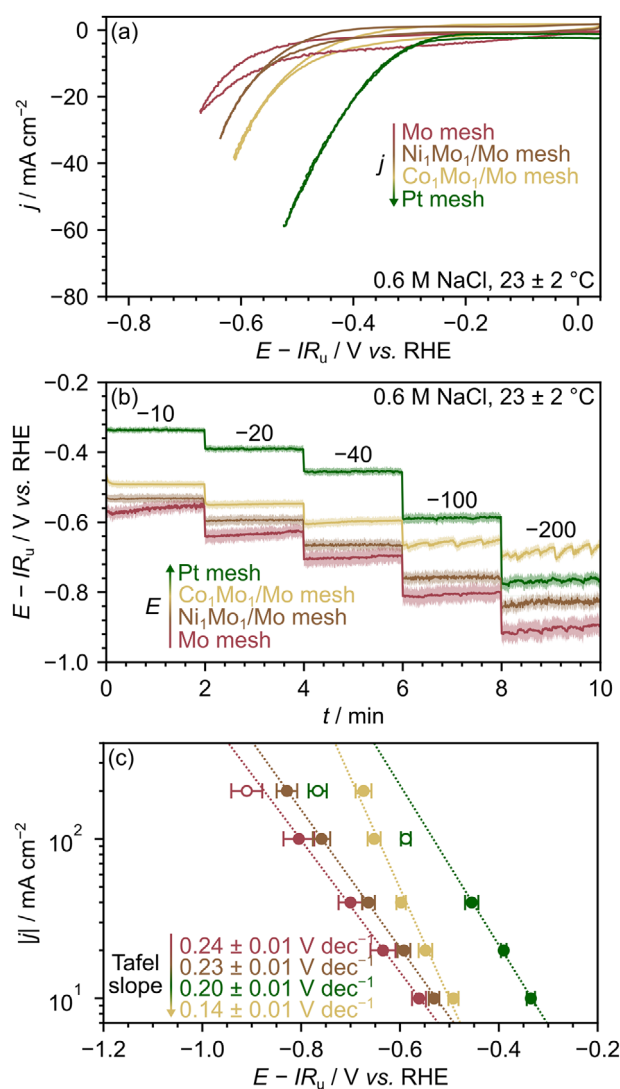


FIGURE 5 | Initial HER activity of the molybdenum-based cathodes and Pt mesh in 0.6 M NaCl. (a) Stabilized cyclic voltammograms (scan rate, $v = 0.010 \text{ V s}^{-1}$; third scans), (b) chronopotentiograms at current densities shown in the plot, and (c) the HER polarization plots derived from the data in panel b (symbols are experimental data; lines are linear fits within ranges of observed linearity (●), the inverse slopes of which represent Tafel slopes shown in the figure) for $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh (golden), $\text{Ni}_1\text{Mo}_1/\text{Mo}$ mesh (brown), Mo mesh (wine), and Pt mesh (dark green). Data in panels b–c are shown as mean (lines, symbols) $\pm$ standard deviation (shading, error bars) derived from testing $n = 3$ independent samples of each type. Currents are normalized to the geometric surface area of the electrodes (1 cm^2); potentials were manually IR_u -corrected post-measurements. Experiments were undertaken at $23 \pm 2^\circ\text{C}$ and under stirring at 1600 rpm by a Teflon-lined bar.

and cathode (Figure 6a). The cathode was a $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh described above (Figure 5). The anode was a DSA substrate coated with a dense layer of $\text{Co}_3\text{Fe}_1[\text{B}]_x[\text{OH}]_y$ to minimize exposure of the iridium-ruthenium-oxide coating to the electrolyte solution (Figure S21). While these noble metals are nominally not required and are in fact undesirable in the electrolysis of seawater due to their high preference for the CER, we opted to use the DSA as the most robust substrate that would not undergo any significant corrosion during operation in a chloride-containing electrolyte

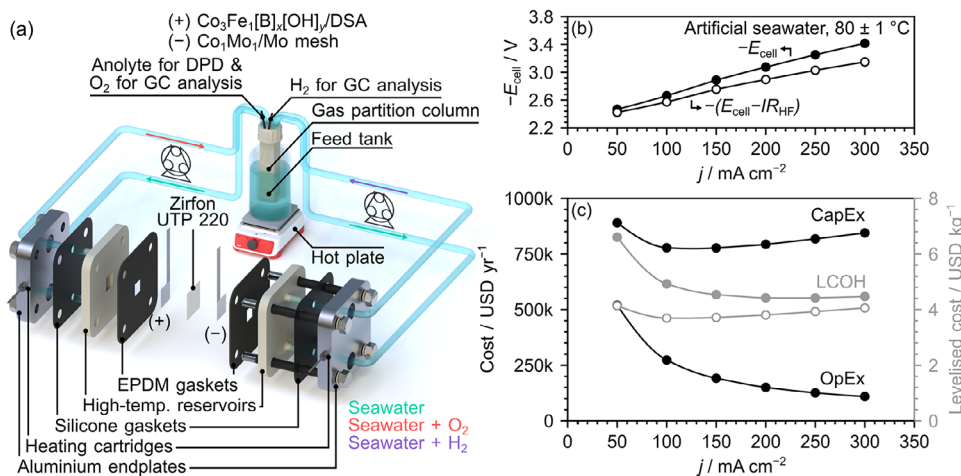


FIGURE 6 | Direct artificial seawater electrolysis within a zero-gap electrolytic cell at $80 \pm 1^\circ\text{C}$. (a) An exploded schematic of an electrolyzer depicting Co₃Fe₁[B]_x[OH]_y brush-coated onto a DSA anode substrate and Co₁Mo₁ electrodeposited onto a Mo mesh cathode substrate (both 1 cm × 1 cm), a Zirfon UTP 220 separator, hermetically sealed with silicone and ethylene propylene diene monomer (EPDM) gaskets. A peristaltic pump circulated artificial seawater (25 mL min⁻¹) from a feed tank to both compartments, as shown by teal arrows, while red and purple arrows indicate the return flow of the artificial seawater and evolved gases. A partially submerged gas partition column prevents mixing of O₂ and H₂. (b) Polarization curve with the filled (●) and empty (○) symbols represent $-E_{\text{cell}}$ before and after IR_{HF} -correction. (c) Breakdown of the levelized cost of hydrogen (LCOH) from direct artificial seawater electrolysis under base-case assumptions, including CapEx and OpEx, using the electricity cost of USD20 MWh⁻¹ (black). The grey filled (●) and empty (○) symbols indicate the actual LCOH using DSA substrate and the projective LCOH using stainless steel mesh substrate. Calculations are provided in the Supporting Excel Spreadsheet.

solution for multiple days at elevated temperature and positive potentials [46]. A more practical design would require replacing a DSA with a more cost-effective substrate coated with corrosion-resistant material, for example doped TiO₂ or SnO₂, which will require future optimization.

First, we assessed the short-term performance of the direct seawater electrolyzer in artificial seawater prepared using a commercially available salt mix (Table S10) at an elevated temperature of $80 \pm 1^\circ\text{C}$. The resulting current density vs. cell voltage dependence demonstrated an apparently linear behavior with a slope of $3.8 \Omega \text{ cm}^2$ (Figure 6b). However, the high-frequency resistance of the cell (R_{HF}) within the examined current density range was ca. $0.9 \Omega \text{ cm}^2$, indicating that the major inefficiency results from the kinetics of the half-reactions, as expected based on the data discussed above (Figures 2 and 5).

Considering the relatively high energy requirement of the electrolyzer, which was not unexpected for the direct seawater electrolysis and consistent with other studies [58, 59], we aimed to identify an operating current density that would present the most balanced combination of the capital (CapEx) and operational expenditure (OpEx) of the device for the extended stability tests. To do so, we created a technoeconomic model of a theoretical 1 MW plant operating over a 30-year lifespan, based on the previous study [60]. The model incorporated a 10% performance degradation over the plant lifetime to account for system ageing and efficiency losses, along with a 10% depreciation of the plant's capital value. CapEx was estimated based on the data provided in a report from the International Renewable Energy Agency (IRENA) [61], covering stack components, balance of plant, and

diaphragm/electrode package. OpEx included electricity costs, labor (0.4% of CapEx), routine maintenance (2.5% of CapEx), and auxiliary (1% of CapEx). Water-related expenses were excluded from the analysis due to the use of seawater as the feedstock instead of pure water. The model is available in the Supporting Excel Spreadsheet.

The CapEx and OpEx values were calculated as a function of the operating current density and were used to determine the levelized cost of hydrogen (LCOH) assuming the electricity price of USD20 MWh⁻¹ based on a recent IRENA report [61] (Figure 6c). The obtained data suggest that operating the electrolyzer described herein at current densities above 100 mA cm^{-2} would produce a marginal reduction in the LCOH, which levels off at approximately 200 mA cm^{-2} at a value of ca. USD4.4 kg⁻¹, which is expectedly above the commercialization target of USD2.5 kg⁻¹ [62]. It should be noted that a significant contribution to this high cost is made by Ir and Ru used in the DSA substrate. The reason behind the use of this substrate herein was exclusively to prevent substrate-dependent artefacts during long-term operation, because the electrolyte solution can still wick towards the underlying anode substrate through pinholes, microcracks, or exposed edges in the coating and trigger corrosion. As noted above, the DSA is one of few directly available electrodes that are stable against corrosion during oxidation of saline water, but it can be potentially replaced with more cost-effective materials, for example based on titanium, niobium, or antimony. Assuming this replacement is achieved, the hypothetical LCOH would be USD3.7 kg⁻¹ at 100 mA cm^{-2} using stainless steel mesh substrate. Hence, we concluded that this value of current density provides optimal conditions for the extended durability tests at this stage.

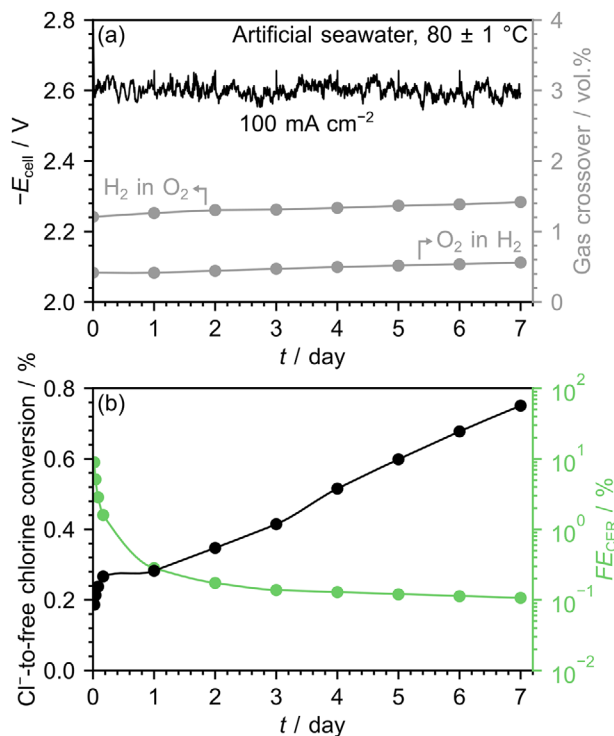


FIGURE 7 | Extended seawater electrolysis at 100 mA cm^{−2} in artificial seawater at 80 ± 1 °C. (a) Evolution of the potential of the cell shown in Figure 6a (black), gas crossover (grey), (b) Cl[−]-to-free chlorine conversion (black) and of FE_{CER} (green) over a week-long electrolysis.

2.4 | Extended Direct Artificial Seawater Electrolysis Tests

The electrolyzer maintained a stable cell voltage of ca. −2.6 V and 80 ± 1 °C in artificial seawater throughout seven days of a chronopotentiometric test at 100 mA cm^{−2} (Figure 7a). The Zirfon UTP 220 separator effectively minimized evolved gas crossover, maintaining H₂ in O₂ and O₂ in H₂ levels at ~1.3 and ~0.5 vol.% (Figure 7a; Table S11). These values were slightly higher than those typically measured in alkaline water electrolyzers at comparable current densities [63, 64], but remained within the safety limits recommended by the International Organization for Standardization (ISO), namely below 2.0 vol.% for H₂ in O₂ and 1.6 vol.% for O₂ in H₂ [65]. Only H₂ and O₂, along with traces of N₂, were detected in the anode gas by gas chromatography, confirming that any evolved chlorine was rapidly and quantitatively converted into dissolved HOCl/CIO[−] (Figure S23). Further, we quantified the amount of chloride during the electrolysis within a feed tank volume of 80 mL initially containing 45 mmol Cl[−]. By the end of the test, only 0.7 mmol Cl[−] was consumed, corresponding to a Cl[−]-to-free chlorine conversion of 0.8% (Figure 7b; Table S13). The FE_{CER} declined gradually during the first day, decreasing from 8.9% at 30 min to 1.6% at 4 h, falling below 0.5% after 24 h, and stabilizing around 0.1% for the remainder of the test (Figure 7b; Table S14). The FE_{OER} calculated from the gas chromatography data produced consistent values (Table S12). These results demonstrated that the direct seawater electrolyzer presented herein selectively catalyzes the OER instead of the CER.

After 7 days of the direct artificial seawater electrolysis, the Co₃Fe₁[B]_x[OH]_y/DSA anode was characterized by SEM-EDS and ICP-MS (the latter was done by digesting the electrode in 2 wt.% HNO₃). The Co₃Fe₁[B]_x[OH]_y-derived nanoparticles largely retained their adhesion to the DSA substrate (Figure S22 and Table S16). ICP-MS analysis demonstrated a boron content of ca. 3.1 at.% (with respect to the overall Co+Fe+B content) after long-term seawater electrolysis, which was approximately one-third of the B content in the as-synthesized material (Table S16). This result demonstrates that a significant portion of boron was retained within the catalytically active form of the material. When considered together with the DFT results (Figure 1), characterization of the anode catalyst under model conditions (Figure 4), and the significantly suppressed kinetics of the CER (Figure 7b), one might propose that the presence of boron-based species, likely in the form of surface borates, supports the high selectivity of the Co₃Fe₁[B]_x[OH]_y-derived anodes for the OER during electrolysis of artificial seawater.

The hydroxide formation on the Co₁Mo₁/Mo mesh cathode was examined by XRD, SEM-EDS, and ICP-MS. The XRD pattern displayed low-intensity broad peaks of Ca(OH)₂ around 22° and 40°, Mg(OH)₂ at ~45°, and CaCO₃ at approximately 34° (Figure 8a). The presence of CaCO₃ resulted from the reaction between Ca²⁺ and carbonate species naturally present in artificial seawater or from ambient air. These low-solubility compounds appeared as fine surface deposits rather than large agglomerates obstructing the mesh structure (Figure 8b). Complete pore blockage would have reduced the electrochemically active surface and hindered H₂ gas release, resulting in increased cell voltage, which was not observed in the extended chronopotentiogram (Figure 7a). Elemental EDS mapping suggested that the Mg and Ca concentrations on the cathode after the one-week test were ca. 8.5 and 4.3 at.% relative to the overall detected elements (Figure 8c; Table S16). More precise quantification of Mg²⁺ and Ca²⁺ by ICP-MS produced values of 2.4 and 0.4 at.% with respect to the overall metal content, respectively (Figure 8c; Table S16). The higher level of Mg precipitation as compared to Ca was due to the higher Mg²⁺ concentration in artificial seawater (53 vs. 8 mmol kg^{−1}) and notably lower solubility product of Mg(OH)₂ ($K_{\text{sp}} = 5.6 \times 10^{-12}$) compared to CaCO₃ (3.3×10^{-9}) and Ca(OH)₂ (5.0×10^{-6}) [44].

Overall, both electrodes exhibited stable performance and appreciable activity throughout the extended test, with no noticeable degradation. The electrolyzer yielded only ca. 0.01 moles of Cl₂ per mole of H₂ produced during the week-long artificial seawater electrolysis. In other words, the anode delivered near-complete OER selectivity, virtually eliminating the unwanted CER in this context.

3 | Conclusion

In summary, the present work aimed to contribute to the development of the direct seawater electrolysis technologies by demonstrating a zero-gap electrolytic device operating at a practical current density and temperature under seawater-representative conditions. The electrolyzer used an OER-selective anode, derived from the mixed cobalt-iron boride/borate/hydroxide material, and a zero-gap design that mitigated build-up of insoluble

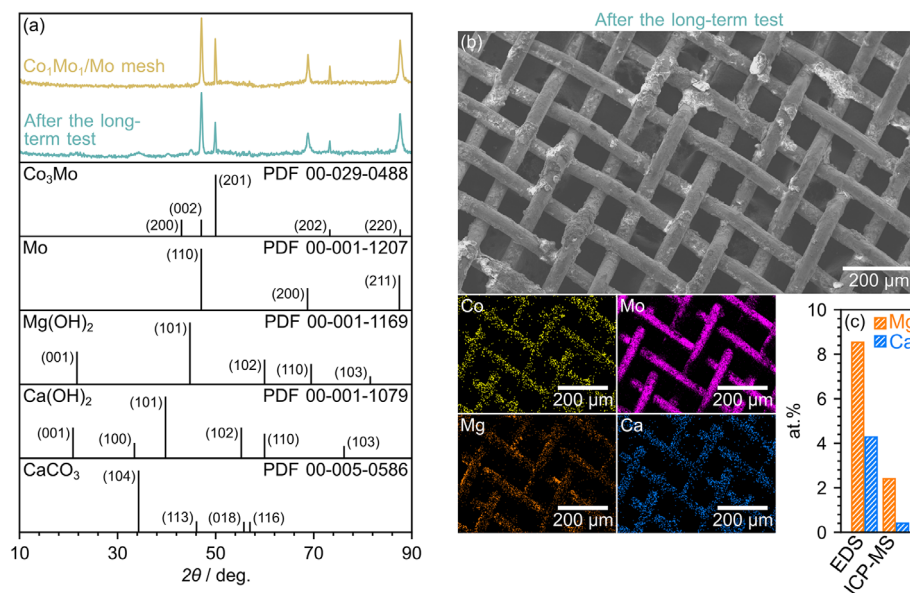


FIGURE 8 | Characterization of the cathode after one week of the artificial seawater electrolysis. (a) XRD patterns normalized to the intensity of the Mo(110) reflection, (b) low magnification scanning electron micrograph with energy-dispersive X-ray spectroscopy elemental mapping for Co, Mo, Mg, Ca, and (c) atomic fractions of Mg (orange) and Ca (blue) with respect to the overall detected metals by EDS and ICP-MS for the $\text{Co}_1\text{Mo}_1/\text{Mo}$ mesh cathode before (golden) and after (teal) the direct artificial seawater electrolysis experiment at 100 mA cm^{-2} in artificial seawater at $80 \pm 1^\circ\text{C}$ shown in Figure 7. In panel a, data are compared to the tabulated positions and relative intensities of the relevant reference materials shown as black vertical lines.

hydroxides and carbonates at the cathode while maintaining satisfactory purity of the evolved gases. The OER selectivity was most likely provided by the presence of borate species, which were suggested by DFT calculations to facilitate the OER while disfavoring the CER. Meanwhile, the continuous H^+ flux from the anode limited local OH^- build-up at the cathode, suppressing the formation of insulating hydroxide layers [44]. The oxygen vs. chlorine evolution selectivity achieved herein compared favorably with previously reported direct seawater electrolyzers (Table S17). While low FE_{CER} has also been reported in prior studies, its quantification was sometimes inferred from proxy measurements or assumptions, and gas crossover was not consistently reported, complicating quantitative comparison of the electrolyzer performance. In contrast, the present study quantified the FE_{CER} and gas crossover in a time-resolved manner over extended period of operation as well as the degree of the cathode scaling, aiming to provide a more rigorous assessment of the performance under seawater-relevant conditions.

The cell voltage demonstrated herein was higher [58, 59, 66] or comparable [67] to those reported in the previous studies on direct seawater electrolyzers (Table S17), which directly contributes to the LCOH. The latter, calculated for the electrolyzer described in this work, was higher than the commercialization target, but can be decreased substantially by removing the DSA substrates that are, theoretically, not required in the final design. Future improvements can arise from enhancing the active surface area of the electrodes, as compared to the relatively low-surface-area meshes explored herein. However, it should be recognized that direct seawater electrolysis is likely to be inherently limited in energy efficiency, defined by the pH and natural composition of this electrolyte solution. While improved cell voltages might be possible with the use of polymer cation and anion exchange

membranes [58, 59, 66], the high cost of these materials would significantly increase the CapEx of the electrolyzer. Besides, the durability of these electrolytes under seawater conditions at high temperatures and current densities is yet to be proven, while frequent replacement would result in higher OpEx. Under these considerations, the direct seawater electrolysis might be most practical when using the cheapest cell components and when powered by renewable energy sources providing very low or even negative electricity prices only [68–70]. Combined with proximity to the coastline, these conditions could further reduce the LCOH, making direct seawater electrolysis a more competitive technology.

4 | Experimental Section

4.1 | Chemicals and Materials

The work used the following chemicals and solvents: cobalt(II) chloride hexahydrate (98%, Sigma-Aldrich), cobalt(II) nitrate hexahydrate (98%, Sigma-Aldrich), iron(III) chloride (98%, Sigma-Aldrich), iron(II) chloride tetrahydrate (98%, Sigma-Aldrich), manganese(II) chloride tetrahydrate (98%, Sigma-Aldrich), manganese(II) sulphate monohydrate (98%, Merck), nickel(II) chloride hexahydrate (98%, Sigma-Aldrich), nickel(II) nitrate hexahydrate (98%, Sigma-Aldrich), sodium molybdate dihydrate (99%, Sigma-Aldrich), sodium tungstate dihydrate (99%, Sigma-Aldrich), tin(IV) chloride (98%, Sigma-Aldrich), ammonium chloride (99%, Merck), sodium borohydride (99%, Sigma-Aldrich), sodium carbonate (99%, Sigma-Aldrich), sodium chloride (99%, Merck), sodium hydroxide (99%, Merck), sodium hypochlorite (95%, Sigma-Aldrich), iodine (99%, Sigma-Aldrich), polyvinylidene fluoride (PVDF; avg. $M_w \sim 534,000$ by GPC, Sigma-Aldrich), *N*-Methyl-2-pyrrolidone (NMP; 99%,

Sigma-Aldrich), 30% hydrogen peroxide (EMSURE, Merck), sulfuric acid (98%, Ajax Finechem), nitric acid (70%, Ajax Finechem), oxalic acid (99%, ChemSupply), ethanol (absolute, Ajax Finechem), isopropanol (AR grade, Ajax Finechem), Nafion dispersion (5 wt.%, Fuel Cell Store), *N*, *N*-diethyl-*p*-phenylenediamine (DPD) Cl₂ Spectroquant test kit (MQ100, Merck), dimensionally stable anode mesh (DSA, a 3 µm-thick layer of mixed Ir and Ru oxides on a Ti mesh support, Hebei Boni Tech Co., Ltd.), platinum mesh (Fuel Cell Store), platinum wire (Goodfellow Cambridge Ltd), molybdenum mesh (Hebei Boni Tech Co., Ltd.), TEC 8 fluorine-doped tin(IV) oxide (FTO) coated glass slides (8 Ω sq⁻¹, Greatcell Solar Materials Pty Ltd), and nickel wire (Goodfellow Cambridge Ltd).

Artificial seawater salt mixture (ASTM D1141-98) was purchased from Lake Products Company LLC. Deionized water (measured resistivity of 18.2 MΩ cm at 23 ± 2°C) was derived from the Sartorius Arium Comfort I Ultrapure water system H2O-I-1-UV-T and was used in all procedures requiring H₂O.

4.2 | Materials Synthesis

Transition metal borides were synthesized via chemical reduction of metal salts dissolved in water with sodium borohydride. For Co₃Fe₁[B]_x[OH]_y, 2.25 mmol cobalt(II) chloride hexahydrate and 0.75 mmol iron(III) chloride were dissolved in 10 mL H₂O. Separately, 9 mmol sodium borohydride was dissolved in 10 mL of aqueous 0.1 M sodium hydroxide. Both solutions were purged with Ar while cooled on ice for 30 min to suppress the decomposition of borohydride and resulting borides. The sodium borohydride solution was added dropwise to the metal precursor solution, forming a black suspension. The precipitate was thoroughly washed with water, centrifuged, and dried for ca. 14 h in a vacuum oven at ca. 60°C. Syntheses of Co[B]_x[OH]_y, Fe[B]_x[OH]_y, Mn[B]_x[OH]_y, and Ni[B]_x[OH]_y were performed similarly, using 3 mmol of the corresponding metal salts: cobalt(II) chloride hexahydrate, iron(II) chloride tetrahydrate, manganese(II) chloride tetrahydrate, and nickel(II) chloride hexahydrate, respectively.

Cobalt-iron layered double hydroxides were synthesized via a hydrothermal method. Briefly, 2.25 mmol cobalt(II) chloride hexahydrate and 0.75 mmol iron(III) chloride were dissolved in 40 mL H₂O. Separately, 3.5 mmol sodium hydroxide and 1.8 mmol sodium carbonate were dissolved in 40 mL H₂O. The two solutions were mixed, purged with Ar, transferred to a Teflon-lined autoclave, and heated at 90°C for 12 h. The precipitate was thoroughly washed with water, centrifuged, and dried for ca. 14 h in a vacuum oven at ca. 60°C.

Manganese-molybdenum oxides were synthesized following the procedures reported in the literature [49, 50] by electrodeposition in a two-electrode configuration using a DSA mesh (1 cm × 1 cm) as an anode positioned ca. 2 cm away from a Pt mesh (2 cm × 2 cm) cathode. The electrolyte solution was prepared by dissolving 8 mmol manganese(II) sulphate monohydrate, 0.12 mmol sodium molybdate dihydrate, and 0.24 mmol sodium tungstate dihydrate or tin(IV) chloride in 40 mL H₂O. Deposition was performed at 90°C under a constant current density of –60 mA cm⁻² under continuous stirring at 400 rpm provided by a Teflon-lined stirring bar (Ø 0.5 cm × 1.5 cm) in three 30-min-

long steps, using a fresh electrolyte solution for each step. The resulting samples were rinsed three times with water and dried over ca. 14 h in a vacuum oven at ca. 60°C.

4.3 | Working Electrode Preparation

Working electrodes were prepared using glassy carbon rotating disk electrodes (GC RDE; Ø 0.5 cm, ALS Co., Ltd.) or freestanding mesh substrates. GC electrodes were polished sequentially with 1.0, 0.3, and 0.05 µm alumina powders (Alfa Aesar) to a mirror finish, followed by 30 s sonication in a 1:3 vol. water : ethanol mixture.

FTO slides (10 cm × 10 cm) were cut into pieces (0.4 cm × 1.5 cm) using a diamond-tipped glass cutter and cleaned in an Elmasonic S300H ultrasonication bath (1500 W, Elma Ultrasonics) sequentially with 2% Hellmanex III surfactant aqueous solution (Hellma), water, and ethanol for 20 min in each solvent. The slides were then dried under N₂ flow and further plasma-treated for 5 min (1000 mTorr, Harrick plasma cleaner). The electroactive geometric area was defined using Kapton polyimide tape (0.4 cm × 0.5 cm).

Mo mesh substrates were immersed in 10 wt.% oxalic acid at 80°C for 1 h. DSA substrates were cleaned by galvanostatic oxidation at 15 mA cm⁻² for 15 min in quiescent 0.1 M H₂SO₄ under ambient conditions. Pt mesh was pre-treated with 3:1 vol. H₂SO₄(conc.) : H₂O₂(30 wt.%) solution.

GC electrodes were modified with catalysts by drop-casting. The catalyst inks were prepared by sonicating a dispersion of 5 mg of a catalyst in 1 mL of a solvent mixture comprising 0.72 mL water, 0.25 mL isopropanol, and 0.03 mL of 5 wt.% Nafion dispersion for 30 min. Sonication was conducted using a Meinhardt Ultrasonics (40 Hz, 50 W) ultrasound setup equipped with a cooling jacket to prevent heating of the dispersions. The resulting ink was drop-cast in 2.5 µL aliquots onto clean and dry GC electrodes (0.25 mg cm⁻² loading) and dried in an oven at 60°C for 1 h.

FTO electrodes were modified by electrophoresis following the reported procedure [71]. The dispersion was prepared by adding 25 mg of catalyst powder, ground in an agate mortar, to 8 mL of acetone. The mixture was then sonicated for 3 h using the ultrasonic setup mentioned above. Subsequently, 2 mg of iodine was added, and the dispersion was sonicated for an additional 3 min. Iodine reacts with acetone through keto-enol tautomerism to produce protons, which adsorb onto the surface of the suspended catalyst. When a negative potential is applied to the substrate, the electric field drives the positively charged catalyst particles to migrate and deposit onto its surface [71]. Electrophoresis was undertaken under ambient conditions, with the FTO electrodes as the cathode and coiled Ni wire (Ø0.1 cm × 7.5 cm) as the anode, both immersed in the air-saturated catalyst dispersion. A potential difference of 10 V was applied between the electrodes for 10 min, while the dispersion was stirred at 400 rpm using a Teflon-lined stirring bar (Ø 0.3 cm × 0.8 cm).

Freestanding anodes were fabricated by brush-coating a paste of the catalyst. The paste was prepared by dispersing 5 mg of the Co₃Fe₁[B]_x[OH]_y powder in 0.95 mL isopropanol and 0.05 mL of

8 wt.% PVDF in NMP binder by sonication for 30 min using the same setup as above. The whole volume of the resulting paste was brush-coated onto a freshly cleaned DSA substrate in portions of ca. 0.1 mL with drying at 60°C for 10 min in between, followed by ca. 14 h drying in a vacuum oven at 60°C.

Freestanding cathodes were prepared via electrodeposition in a three-electrode setup using Mo mesh (1 cm × 1 cm) as the working electrode, a saturated calomel electrode (SCE, Latech) as the reference electrode, and Pt mesh (2 cm × 2 cm) as the counter electrode. The Co₁Mo₁ deposition solution consisted of 2 mmol cobalt(II) nitrate hexahydrate, 2 mmol sodium molybdate dihydrate, 40 mmol ammonium chloride, and 20 mmol sodium chloride in 40 mL water. Deposition was carried out at −1.3 V vs. SCE for 15 min and stirred at 400 rpm using a Teflon-lined stirring bar (Ø 0.5 cm × 1.5 cm). Ni₁Mo₁ deposition was performed similarly by replacing cobalt(II) nitrate hexahydrate with an equimolar amount of nickel(II) nitrate hexahydrate. The samples were rinsed three times with water and dried over ca. 14 h in a vacuum oven at 60°C.

4.4 | Reversible Hydrogen Electrode

A reversible hydrogen electrode (RHE) was prepared by electroplating a Pt wire (Ø0.1 cm × 7.5 cm) in 10 mM chloroplatinic acid at −10 mA cm^{−2} under ambient conditions, forming a porous Pt black deposit as per the reported procedures [72]. The resulting Pt/Pt electrode was then immersed in H₂-saturated 0.6 M NaCl or artificial seawater and used to calibrate the Hg|Hg₂Cl₂|KCl_{sat} (SCE, Latech) reference electrode. The SCE potential was measured as 0.626 ± 0.005 in both media at ambient temperature (hereinafter 23 ± 2°C).

4.5 | Electrochemical Procedures

Short-term electrochemical measurements were undertaken in a two-compartment Pyrex cell separated by a low-porosity (P4) glass frit, using a standard three-electrode setup with a Biologic VMP-300 electrochemical workstation. Each compartment contained 50 mL of the 0.6 M NaCl electrolyte solution. The Hg|Hg₂Cl₂|KCl_{sat} reference electrode was positioned ca. 5 mm from the working electrode. The auxiliary electrode was Pt mesh (2 cm × 2 cm). The working electrode was a catalyst-modified GC RDE rotated at 1600 rpm using an RDE (ALS Co., Ltd.) setup.

Long-term chronopotentiometry tests were conducted using a custom zero-gap electrolytic cell (scheme shown in Figure 6a) fabricated from Rigid 10K resin (Formlabs) and post-cured at 80°C for 4 h under UV light. Measurements were carried out using a Corrtest CS310X electrochemical workstation. The electrolyzer was fed with artificial seawater using a feed tank volume of 80 mL. The electrolyte solution was used without purification or alkaline precipitation to remove Mg²⁺ and Ca²⁺. Continuous electrolyte solution flow and gas removal were maintained using a BT100-3J peristaltic pump (Longer Precision Pump Co., Ltd.) with chemically resistant Tygon A-60-C tubing (Saint-Gobain) at a flow rate of 25 mL min^{−1}. Experiments were conducted at 80 ± 1°C provided by a monoOne-120 temperature controller and

cylindrical heating cartridges (Three High Co., Ltd.) installed into the aluminium endplates. The seawater feed tank was independently heated using an IKA RCT basic hot plate and stirred at 400 rpm using a Teflon-lined stirring bar (Ø0.5 cm × 1.5 cm), with temperature regulated by an integrated thermocouple wrapped in a PVDF shrink-wrap. Water was periodically replenished into the electrolyte feed tank to compensate for the evaporation and consumption by electrolysis.

Uncompensated resistance (R_u) was determined by electrochemical impedance spectroscopy recorded at the stabilized open-circuit potential, using 10 mV amplitudes over a frequency range of 100 kHz to 0.1 Hz at both the beginning and end of each experiment. $I R_u$ compensation was applied manually during data processing where required.

Data with error bars represent an average ± one standard deviation derived from experiments conducted using three independently synthesized samples of the same type.

Electrochemical cells and all glassware were cleaned prior to use by overnight soaking in freshly prepared 1:1 vol. H₂SO₄(conc.) : H₂O₂(30 wt.%) solution, followed by thorough rinsing with copious amounts of water.

4.6 | Quantification of Free Chlorine

Free chlorine (HOCl/OCl[−]) was quantified using the US Environmental Protection Agency's (USEPA) approved colorimetric method [73] with an *N*, *N*-diethyl-*p*-phenylenediamine (DPD, Merck) Cl₂ Spectroquant test kit and a Cary 60 UV-vis spectrophotometer (Agilent Technologies). Calibration in 0.6 M NaCl electrolyte (Figure S1) was performed using NaClO at concentrations ranging from 1 to 50 µM, derivatized by adding 15 mg of the DPD powder and vigorously shaking for 30 s to induce the formation of a Wurster dye with a distinct magenta color [73]. The UV-Vis spectra were recorded within 2 min of adding DPD in a 1 cm quartz cuvette at 160 nm s^{−1}. A molar absorption coefficient (ε) of the Wurster dye measured herein was 0.013 ± 0.001 µM^{−1} cm^{−1} at 515 nm (A_{515}), consistent with the standardized procedure. Electrolyzed samples were analyzed upon a minor dilution, typically 10-fold, with 0.6 M NaCl following the same procedure as the standard solutions.

The CER faradaic efficiency (FE_{CER}) was calculated using the following equation:

$$FE_{CER} = C_{freeCl} \times \text{dilutionfactor} \times V_{total} \times 2 \times F / Q \quad (1)$$

where C_{freeCl} , V_{total} , F , and Q are the free chlorine concentration in the solution (M), the volume of the electrolyzed anolyte (L), the Faraday constant (96485.3 C mol^{−1}), and the total passed charge (C), respectively.

4.7 | Computational Methods

Calculations were performed using the density functional theory (DFT) within the generalized gradient approximation (GGA), using the revised Perdew-Burke-Ernzerhof (RPBE) functional

with Pade approximation [74] with a plane-wave cut-off energy of 400 eV. Bulk structures were fully optimized with the following stringent convergence criteria: energy and force convergence limit equal to 10^{-5} eV atom⁻¹ and $|0.001|$ eV Å⁻¹. The Brillouin zone (periodic boundary conditions) was sampled using the Monkhorst-Pack scheme [75], increasing the number of *k*-points until electronic energy differences were below $|0.1|$ eV.

Slab models were constructed with a vacuum width of 15 Å to prevent interactions between periodic images. Thus, for the modelling of the clean surfaces and adsorbates, energy and force convergence limits were set to 10^{-4} eV atom⁻¹ and $|0.01|$ eV Å⁻¹, with a set of $3 \times 3 \times 1$ *k*-points. In all cases, explicit dispersion correction terms to the energy were accounted for using the D3 method with the standard parameters programmed by Grimme and co-workers [76, 77]. Spin polarization was included in all calculations.

Optimization and vibrational frequency calculations were performed using the Vienna Ab Initio Simulation Package (VASP, version 5.4.4) [78–81]. Solvent effects were modelled using the VASPsol implicit solvation model, which accounts for electrostatic, cavitation, and dispersion interactions between solute and solvent [82, 83].

4.8 | Physical Characterization

X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance Eco Diffractometer equipped with a LynxEye XE 1D energy-discriminating strip detector and a 980 W Co-anode X-ray source (35 kV, 28 mA) with Fe K_β filtering. Data were collected at ambient temperature with a step size of 0.02° and a count time of 1 s per step. Catalyst powders were dispersed in 1 mL ethanol by 30 min sonication and drop-cast onto a dispersion-specific sample holder.

Scanning electron microscopic (SEM) and energy dispersive X-ray spectroscopic (EDS) analysis were conducted using an FEI Quanta 3D FIBSEM, FEI Nova NanoSEM 450FEGSEM, and a JEOL IT800 SHL FEGSEM equipped with an Oxford Instruments Ultim Max 170 mm² EDS detector operated at 15 kV with a 10 mm working distance. Powder samples were dispersed in ethanol and drop-cast onto conductive silicon wafers (ca. 3 mm × 3 mm), which were mounted to SEM stubs using double-sided carbon tape. Prior to analysis, the samples on silicon wafers were sputter-coated with a thin layer of nanoparticulate iridium (10 s at 4 W) to improve conductivity; electrical contact was provided using copper tape. SEM imaging was conducted at 15 kV with a probe current of 9 nA. For samples grown directly on substrates, no additional conductive coatings were applied; they were mounted directly onto flat or vertical SEM stubs using double-sided carbon tape.

Transmission electron microscopic (TEM) analysis was performed on an FEI Tecnai G2 T20 with an LaB₆ emitter and Bruker Esprit 2.0 software. Samples were dispersed in *n*-butanol, drop-cast onto holey-carbon-coated copper grids (LC300Cu25 Emgrid), and dried for 12 h prior to imaging. TEM was operated at 200 kV with a beam current of 4.78 μA.

X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific Nexsa Surface Analysis System equipped with a hemispherical analyzer operating under ultra-high vacuum (10^{-8} – 10^{-9} mbar). A monochromatic Al K_α X-ray source (1486.6 eV) was used at 72 W (12 kV × 6 mA) with a 45° incident angle and a spot size of 200 μm × 400 μm. A low-energy dual-beam (ion and electron) flood gun provided charge neutralization. Survey scans were acquired at 200 eV pass energy with a 1 eV step size and 10 ms dwell time. High-resolution scans were collected at 50 eV pass energy with a 0.1 eV step size and 50 ms dwell time, yielding a typical Ag 3d_{5/2} FWHM of 0.83–0.84 eV. Measurements were taken at a nominal photoelectron emission angle of 0° relative to the surface normal. For rough surfaces, actual emission angles ranged from 0° to 90°, corresponding to a sampling depth up to ~10 nm. Data were processed using Advantage software version 5.9902. Elements were identified from survey spectra, and all binding energies were referenced to the aliphatic C 1s peak at 284.8 eV. Two spots per sample were probed to confirm the reproducibility.

X-ray absorption (XAS) experiments at Co K- and Fe K-edges were performed at the XAS beamline (12-ID) of the Australian Synchrotron, using a multipole wiggler source with a 3.0 GeV electron beam and a 200-mA beam current (maintained in top-up mode). Spectra were acquired in fluorescence mode using a 100-element fluorescence detector with Si(111) monochromators and focusing optics [84]. Thin film electrocatalysts deposited on FTO or carbon fiber paper were exposed to the beam. Energy calibration was performed using metal foils measured either simultaneously or directly after the analysis of the catalyst. The Co K-edge was referenced to the first inflection point of Co foil (7709 eV), and the Fe K-edge to that of Fe foil (7112 eV).

In situ XAS measurements were conducted using a hermetically sealed spectroelectrochemical cell [85] with continuous electrolyte flow maintained by a BT100-2J peristaltic pump (Longer Precision Pump Co., Ltd.) at a 5 mL min⁻¹ rate to prevent O₂ bubble accumulation. A Teflon fabric-reinforced Nafion N324 membrane separated the working and auxiliary electrodes. The cell used a platinized titanium grid auxiliary electrode and a hermetic Ag|AgCl|KCl (3.4 M) LF-1-100 reference electrode (Innovative Instruments). The working electrodes were fabricated by drop casting ca. 0.05 mg cm⁻² of the material (using the same ink as for the GC electrode) on a SpectraCarb carbon fiber paper laminated into PET and laser-defined to an 8 mm diameter area exposed to the electrolyte solution [86].

Raw data obtained from the beamline were processed using Sakura [87], and further analyzed using Artemis [88] and PySpline [89].

Gas chromatography (GC) analysis was performed using an SRI Instruments 8610C Gas Chromatograph system with Ar as the carrier gas. Two molecular sieve 5 Å columns (80/100, 2.0 m × 1/8" OD × 2.0 mm ID, Restek Corp.) connected in series were used to separate N₂, O₂, and H₂. Calibration was performed with 0.2 mL injections of high-purity reference gases (N₂ 99.999%, O₂ 99.995%, and H₂ 99.999%) using gas-tight glass syringes. Gas samples were collected in 0.6 L

Supel-Inert multi-layer foil gas bags, pre-evacuated using a vacuum pump, and filled either from gas cylinders or from the anode and cathode outlets of the electrolyzer. The electrolyte feed tank was fitted with a gas partition column and separate vent lines to enable separate evolved gas collection from the anode and cathode over approximately 4 h. Air contamination during syringe withdrawal and injection was evaluated by analyzing pure H₂. The resulting O₂ signal was subtracted from measured O₂ peak areas in the electrolyzer gas samples.

Inductively coupled plasma mass spectrometry (ICP-MS) was performed using a PerkinElmer NexION 2000. For the as-synthesized Co₃Fe₁[B]_x[OH]_y, 10 mg of powder catalyst was dispersed in 10 mL of 2 wt.% HNO₃ and subsequently diluted 1000-fold with 2 wt.% HNO₃. For the Co₃Fe₁[B]_x[OH]_y/DSA anode and Co₁Mo₁/Mo mesh cathode, 1 cm × 1 cm electrodes were cut to 0.5 cm × 0.5 cm, dissolved in 10 mL of 2 wt.% HNO₃ for 48 h, and then diluted 1000-fold with 2 wt.% HNO₃. Internal standards were used to correct for matrix effects and instrumental drift: Li⁶, Sc⁴⁵, and Ge⁷⁴ were used for B¹¹, Fe⁵⁷, and Co⁵⁹ in the anode sample, while Sc⁴⁵, Ge⁷⁴, and Rh¹⁰³ were used for Mg²⁶, Ca⁴³, Co⁵⁹, and Mo⁹⁸ in the cathode sample. Calibration curves were constructed from serial dilutions of stock standard solutions, and background signals from 2 wt.% HNO₃ were subtracted from all measurements.

Author Contributions

ARF co-designed electrolyzer cells, conducted major experiments, undertook UV-vis, SEM-EDS, and XRD, analyzed data, and co-wrote the manuscript. HG co-designed and fabricated cells. LMA conducted DFT calculations. DS collected and analyzed ex situ XAS, in situ XAS, and XPS. TDN performed TEM analysis. MRR conducted ICP-MS analysis. KND performed supporting experiments. RKH supervised and interpreted XAS experiments. DRM and HLD analyzed data and co-supervised the project. ANS conceived of the project, co-designed electrolyzer cells and experiments, analyzed data, and co-wrote the manuscript.

Acknowledgements

Parts of this work were undertaken at the Australian Synchrotron, part of ANSTO, KAUST Supercomputer Laboratory (Shaheen II), Monash Centre for Electron Microscopy, Monash X-Ray Platform, and Monash Chemistry Analytical Platform. The work was financially supported by the Woodside Monash Energy Partnership (project WMEP-SCI-2A-009), Australian Renewable Energy Agency (ARENA; PRO-1082), and Australian Research Council (Future Fellowships to ANS and RKH, FT200100317 and FT230100054; Industry Early Career Fellowship to HLD, IE230100449). LMA is a Ramón y Cajal fellow (ref. RYC2021-030994-I) and acknowledges MCIN/AEI and NextGeneration EU/PRTR for support.

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Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: aenm70819-sup-0001-SuppMat.pdf.

Supporting File: aenm70819-sup-0002-Data.xlsx.