

Bi-Functional Iron-Only Electrodes for Efficient Water Splitting with Enhanced Stability through In Situ **Electrochemical Regeneration**

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Scalable and robust electrocatalysts are required for the implementation of water splitting technologies as a globally applicable means of producing affordable renewable hydrogen. It is demonstrated that iron-only electrode materials prove to be active for catalyzing both proton reduction and water oxidation in alkaline electrolyte solution with superior activity to that of previously established bi-functional catalysts containing less abundant elements. The reported bi-functionality of the iron electrodes is reversible upon switching of the applied bias through electrochemical interconversion of catalytic species at the electrode surface. Cycling of the applied bias results in in-situ electrochemical regeneration of the catalytic surfaces and thereby extends the catalyst stability and lifetime of the water electrolyzer. Full water splitting at a current density of $l = 10 \text{ mA cm}^{-2}$ is achieved at a bias of $\approx 2 \text{ V}$, which is stable over at least 3 d (72 one hour switching cycles). Thus, potential-switching is established as a possible strategy of stabilizing electrode materials against degradation in symmetrical water splitting systems.

1. Introduction

Sources of power based on limited fossil fuel reserves are depleting, and becoming increasingly socially and politically unacceptable due to their environmental and socio-economic impact.^[1-5] Renewable energy sources including wind, geothermal, hydroelectric and solar, which are amongst the most abundant resources on Earth, offer solutions to these issues. Indeed, most countries could cover their total electricity demand using these resources.^[6,7] Recent statistics, however, show that only 18.1% of global energy was supplied by electricity, with the rest of demand being met using chemical fuels.^[8] The globalization of water splitting is a promising route to the sustainable production of the green fuel, hydrogen, and an ultimate goal of the storage of renewable energy. The world's most abundant energy source, solar energy, suffers from the issue of intermittency. Two highly debated approaches in the solar fuels field

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chemical energy using a photovoltaic (PV)electrolyzer^[9,10] system and its direct conversion with a photoelectrochemical (PEC) cell.^[11–13]

The International Energy Agency identified a key obstacle to the widespread implementation of water splitting technologies to be the development of cheap and active materials to catalyze both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which operate under identical and mild conditions with high efficiency and stability.^[14] The most active catalysts of the HER and OER contain precious metals: Pt and RuO₂/IrO₂, respectively,^[15-18] but there is no real possibility to scale up these materials for global demand due to their scarcity. A sustainable and global process will require the use of inexpensive,

widely abundant and nontoxic materials. Figure S1 (Supporting Information) shows the recent cost of transition metal resources and their relative crustal abundance. Rare, high cost elements are suitable for use in luxury items such as catalytic converters in automobiles. Even medium cost-abundance catalysts such as the much investigated HER catalysts, Ni-Mo alloys,^[19,20] as well as Ni₂P,^[21] CoP,^[22] and MoS₂,^[23-26] and the OER catalysts, cobaltphosphate (CoP_i),^[27] nickel-borate (NiB_i),²⁵ and (mixed) metal oxide-hydroxides^[29-32] can still suffer from scalability issues. For example, cobalt constitutes the largest cost in most Li-ion rechargeable batteries (LiCoO₂), which has contributed to significant research into its replacement with iron (LiFePO₄) and manganese (LiMnO₂) analogs.^[33] Approaches to overcome the use of more expensive metals in catalysis include the use of ultra-low concentrations of the active catalyst embedded in a lower-cost matrix^[34] or in this case the identification of active species which contain only Earth-abundant elements.^[30]

Only three transition metals (titanium, manganese, and iron) are truly abundant in Earth's crust (the primary source of metal ores) and within this group, iron is by far the most plentiful. Hence iron is arguably the most attractive element on which to base sustainable catalysts, due to its effectively inexhaustible supply, low toxicity, and negligible environmental impact. Despite this, iron-based catalysts have been relatively underreported and underused, probably due to their notoriety for corrosion.

Iron-based electrodes for either the HER or the OER have been reported,^[35-40] but bi-functionally active iron-only materials in water splitting are unknown. For example, FeP is described as a promising high activity noble-metal-free material

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in acidic solutions (0.5 M H₂SO₄),^[35] however, the applicability of FeP in water splitting is currently limited as it is only active in acidic to neutral pH,^[35–37] where nonprecious metal OER catalysts do not typically operate.^[30] Further, the scalability of phosphide materials is limited by toxicity and availability. Examples of iron oxyhydroxides operating as OER catalysts in alkaline solution are well known and operate in an overpotential range of 0.35–0.5 V,^[38–40] but they have not been reported as HER catalysts. Chlorine oxidized stainless steels were also shown to be OER catalysts at alkaline (1.5 mA cm⁻² at $\eta = 260$ mV) and neutral pH (1 mA cm⁻² at $\eta = 462$ mV).^[41,42] A regenerating ability to enhance stability is also unknown for iron-based water splitting catalysts.

Herein we demonstrate that electrode materials containing only iron as metallic component are bi-functionally active for both water splitting half reactions in alkaline media. Thus, a single and ultra-low cost iron electrode can be used in a symmetrical water electrolyzer and the stability of the iron-only materials can be improved through in-situ electrochemical regeneration of their catalytic surface under reversal of the applied bias. This provides an unprecedented means to repair bi-functional electrodes and provides an elegant solution to stabilize electrode materials that are widely associated with corrosion in aqueous solution. In addition, the use of a bi-functional electrode and this approach to regenerate active catalyst species can help alleviate the instability issues of electrodes in alkaline electrolyzers under conditions of fluctuating currents and gas pressures, which are particularly relevant in the context of a PV-electrolyzer setup. This strategy is specific to bi-functional materials that can catalyze both water splitting half reactions, as otherwise electrolysis would halt during potential cycling.

2. Results and Discussion

2.1. Synthesis and Characterization of Electrode Materials

Iron-only catalytic thin film coatings comprised of iron oxide nanorods (FeO_x), metallic iron nanoparticulates (Fe), and iron sulfide nanocurls (FeS_x) were prepared by simple and scalable aqueous syntheses.^[43] FeO_x was synthesized by a chemical bath deposition (CBD) containing iron(III) chloride and urea, whereas FeS_x was deposited from a CBD containing iron(II) chloride, urea, and thioacetamide, both at 90 °C. The Fe film was prepared by electrochemical deposition from a solution containing iron(II) ammonium sulfate. Full synthetic procedures can be found in the Experimental Section, along with characterization of film thickness and loading (Figure 1, Table S1 in the Supporting Information). Scanning electron microscopy (SEM) images reveal that the three materials have substantially different morphologies (Figure 1). FeO_x consists of nanorods, whereas Fe is an agglomeration of spherical nanocrystals and FeS_x comprises of petal-like nanocurls.

The FeO_x electrodes were determined to be amorphous by powder X-ray diffraction (XRD; Figure S2a in the Supporting Information). The surface composition of the films was also analyzed by X-ray photoelectron spectroscopy (XPS; Figure S3 in the Supporting Information), where peaks at around 710 and 723 eV corresponding to the Fe2p_{3/2} and Fe2p_{1/2} levels in



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Figure 1. Top-view SEM images of FeO_x, Fe and FeS_x films and a commercial Fe foil. Scale bar: 200 nm. Some determined characteristics of FeO_x, Fe, and FeS_x films: film thickness 261, 130, and 520 nm; Fe content 609, 567, and 793 nmol cm⁻², respectively (see the Experimental Section for details).

iron oxide species were found (spin-orbit $\Delta = 13.1$ eV for Fe2p). Deconvolution of the primary Fe2p_{3/2} peak of FeO_x shows two major features at 710.0 and 711.0 eV in agreement with an iron(III) oxide-hydroxide phase (**Figure 2**).^[44]

The metallic Fe films possess a crystalline α -Fe structure with an intense peak at 44.7° 2θ corresponding to the 110 facet and a weaker feature at 82.4° 2θ (211) in the XRD pattern (Figure S2b, Supporting Information). The surface composition, however, consists of iron(0) contained in an iron(III) oxide matrix. The fitted Fe2p_{3/2} XPS spectrum shows a major feature at 709.8 eV for iron(III) oxide and a minor feature at 710.0 eV for the oxide–hydroxide, in addition to a peak at 706.4 eV for metallic iron(0),^[44] which comprises only 5.6% of the surface iron states (Figure 2). This mixed iron(0)–iron(III) oxide surface structure of the electrodeposited Fe film seems to act as a



Figure 2. XPS spectra (baseline corrected) of the $Fe2p_{3/2}$ region of as-prepared FeO_x, Fe, and FeS_x thin film electrodes. The solid (black) line shows the recorded trace and the dashed (blue) line represents the overall peak fit. Colored regions highlight the deconvoluted peaks.

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protection layer to the bulk α -Fe phase, as the material is stably stored in ambient air over many months. For comparison, a commercial iron foil (Alfa-Aesar; Puratronic; 99.995%) rusts considerably in the same timeframe.

The XRD pattern for the FeS_x film shows a strong crystalline feature at 16.8° 2θ , which is in good agreement with the 100 facet of FeS (Figure S2c, Supporting Information). However, the Fe:S ratio of 1:0.7 obtained by energy dispersive X-ray (EDX) analysis of the FeS_x film suggests a sulfur-deficient iron(II) sulfide phase FeS_{1-x} or a mixed sulfide-oxide phase FeS/FeOx. Figure 2 shows the deconvoluted Fe2p3/2 XPS spectrum of FeS_x, where oxide peaks at 709.9 and 710.8 eV similar to FeO_x are observed. Additionally, a peak at 707.8 eV is present, which agrees with the Fe(II)-S environment in FeS.^[45] The S2p spectrum deconvolutes to two spin-orbit doublets (spin-orbit $\Delta = 1.2$ eV for S2p), the major one at 161.4 and 162.6 eV and the other at 163.5 and 164.7 eV (Figure S4, Supporting Information). The former doublet corresponds to monosulfide (S²⁻), while the latter to a less reduced disulfide species (S_2^{2-}) .^[45] The surface composition of FeS_x is therefore likely to be FeS in an iron(III) oxide-hydroxide matrix, but with some (28.0%) of the surface sulfide sites partially oxidized.

2.2. Bi-Functional Electrocatalytic Performance

This series of iron-containing electrodes was tested for catalytic HER and OER activity using linear sweep voltammetry (LSV) under various conditions at room temperature. Aqueous acidic conditions (pH 1) are unsuitable for these materials, as none are stable with respect to dissolution, despite a previous report of iron sulfide activity for HER in 0.5 м H₂SO₄.^[46] Neutral conditions (pH 7, Figure S5 in the Supporting Information) revealed initial HER activity for Fe and FeS_x, but only a stable current for FeS_{x} (Fe loses > 80% of its initial activity within 1 h. Figure S6 in the Supporting Information). For OER catalysis, Fe is unsuitable under neutral conditions as it becomes unstable to dissolution under anodic potential. FeO_x is stable, but requires a very high onset overpotential ($\eta \approx 700$ mV) for OER catalysis. FeS_r is first oxidized where it then has a similarly high overpotential. Hence, acidic and neutral conditions are not suitable for an efficient symmetrical water splitting system using these iron-based electrodes as both anode and cathode.

The best performance was obtained when an alkaline electrolyte solution (0.1 \bowtie KOH, pH 13) was employed. Under these conditions, FeO_x displays a reasonably low overpotential (η at 10 mA cm⁻²) of 400 mV (**Figure 3**a) for OER catalysis, which is comparable to other non-noble metal materials as well as iron-oxyhydroxides.^[39] Strikingly, Fe and FeS_x show a similar activity to FeO_x at an anodic potential. FeS_x undergoes a visible transformation from a black to a yellow film, corresponding to a bulk oxidation of the film. In contrast, the visual appearance of the Fe film remains unchanged suggesting that any oxidation here occurs only at the surface.

In the first cathodic LSV scan, Fe and FeS_x exhibit similar activities, whereas FeO_x requires a much larger η for HER (Figure 3b). Given the comparable activity of all three materials for the OER and both Fe and FeS_x for the HER in alkaline solution, it is unclear from the first scan LSV as to whether the



Figure 3. a) Oxidative and b) reductive LSV scans (First scan; 1 mV s⁻¹; *iR* drop compensated) of as-prepared Fe-containing thin film electrodes (working) in 0.1 \bowtie KOH aqueous electrolyte solution at room temperature. The counter and reference electrodes were Pt mesh and Ag/AgCl, respectively. The dashed lines show consecutive scans of FeO_x.

larger overpotential for HER using FeO_x is the result of inactivity or a more difficult transformation into the catalytically active species. The latter possibility is confirmed by taking successive LSV scans and observing the marked anodic shift of the HER wave with successive scans (Figure 3b and Figure S7 in the Supporting Information).

The potential-time (E-t) traces of a galvanostatic measurement show that all three materials are active for both the HER and the OER with a remarkably similar bias potentials of -0.36 (at -10 mA cm⁻²) and 1.68 V (at +10 mA cm⁻²) versus reversible hydrogen electrode (RHE), respectively, once stabilized (Figure 4). This current density was selected due to its increasing use as an activity benchmark, relevant to achieving 10% efficiency in solar-to-fuels devices.[30] To investigate the reversibility of this bi-functional property, an alternating E-ttrace was recorded, where the current density is periodically switched between + 10 and -10 mA cm^{-2} (Figure 5). Several conclusions can be drawn from the results of these experiments. First, the highly similar catalytic potential of all three materials in both the HER and OER suggests that very similar surface iron species are present during catalysis independent of the initial chemical composition of the electrode. The electrocatalytic response varies according to the ease of conversion





Figure 4. Oxidative (+10 mA cm⁻²) and reductive (-10 mA cm⁻²) *E*-*t* traces of Fe-containing thin film electrodes (working) in 0.1 \times KOH aqueous electrolyte solution at room temperature. The counter and reference electrodes were Pt mesh and Ag/AgCl, respectively.

of the surface species to the active catalysts on the short timescale of the first LSV scan, whereas the most active catalyst is revealed almost instantly in the *E*–*t* trace upon applying a sufficiently high current density due to the rapid interconversion of species. Although the nanostructured FeO_x and FeS_x appear to have a higher surface area than Fe, due to the low conductivity of iron oxides, it is likely that their electrochemically active surface area is much lower than would be expected from the SEM images. Second, η is constant after several alternating cycles between HER and OER. These materials are hence bifunctional and their catalytic phases reversibly interconvertible.

The behavior of the iron-only electrodes is similar to the bi-functional material H_2 –CoCat/O₂–CoCat (in phosphate buffer)^[47] and the more recently reported Ni analog (in borate buffer),^[48] but with superior water splitting performance,



Figure 5. *E*–*t* trace at a constant current density alternating between +10 mA cm⁻² (gray region) and -10 mA cm⁻² (green region) every 0.5 h. The aqueous electrolyte solution was 0.1 \times KOH (pH 13) at room temperature and the working electrodes FeO_x (black), Fe (red), and FeS_x (blue). The counter and reference electrodes were Pt mesh and Ag/AgCl, respectively.



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operating with η = 360 mV (at -10 mA cm⁻²) and 450 mV (at -10 mA cm⁻²) for HER and OER, respectively. CoCat showed HER activity of -2 mA cm^{-2} at $\eta = 385 \text{ mV}$ and OER activity of +1 mA cm⁻² at η = 545 mV.^[47] NiCat showed HER activity of -1.52 mA cm⁻² at $\eta = 452$ mV and OER activity of +0.6 mA cm⁻² at $\eta = 618$ mV.^[48] In these materials, the potential controlled transformation between different catalytic species and morphologies was shown to be responsible for the bi-functional activity. H2-CoCat is reported to contain metallic cobalt active sites in an oxo-hydroxy-phosphate matrix, whereas O2-CoCat, more widely known as CoP_i is a cobalt oxide.^[27,47] The analogous NiCat is similar replacing cobalt and phosphate with nickel and borate.^[48] Unlike these materials, however, here the two catalytic phases are not likely to exchange through solution via a dissolution-deposition mechanism, but instead may convert in the solid state. This is supported by the lack of major morphological change before and after catalysis as observed by SEM (Figure S8, Supporting Information) and further while CoCat and NiCat are metastable with respect to dissolution under open-circuit potential, the iron-based films reported herein are stable in their electrolyte solution. Finally, CoCat and NiCat operate at or close to pH neutral conditions and highcurrent water electrolysis may subsequently suffer from mass transport limitations imposed by the lack of H⁺ and OH⁻ ions. The bi-functional Fe catalysts avoid these limitations, as they are able to function under strongly alkaline conditions.

The bi-functional and reversible activity of FeO_x is also shown to be highly stable over 3 d with only a minor increase in the applied bias for full water splitting during a galvanostatic experiment (≈ 0.02 V, **Figure 6**). This as yet unreported bi-functional property of iron-only materials under alkaline conditions reveals the broad potential to use iron-based materials as catalyst on both anode and cathode in symmetrical water splitting systems. Operating in a reasonable overpotential region^[30] for both the HER and OER half reactions, full water splitting using iron-only materials is possible.



Figure 6. *E*–*t* trace at a constant current density alternating between +10 mA cm⁻² and -10 mA cm⁻² every 1 h for 3 d (black). The red traces show the equivalent *E*–*t* traces without current alternation. The aqueous electrolyte solution was 0.1 m KOH (pH 13) at room temperature and the working electrode was FeO_x. The counter and reference electrodes were Pt mesh and Ag/AgCl, respectively.

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2.3. In Situ Electrochemical Regeneration of Bi-Functional Water Splitting Electrodes

In situ electrochemical regeneration is observed for the prepared FeO_x electrode when potential switching is used. Although these electrodes are stable over the 12 h timescale (Figure 4), over a longer 3 d period degradation of the catalysts is observed when used separately and continuously as HER or OER catalyst as opposed to when potential switching occurs (Figure 6). The HER catalyst gradually decays over 3 d (bias increase of 110 mV), likely due to corrosion or passivation of the surface Fe(0) sites by the electrolyte. The OER catalyst is relatively stable over the same timeframe. The resulting increase in bias for full water splitting with separate FeO_x anode and cathode was therefore 0.11 V. In contrast, when the anode and cathode were reversed every 1 h by potential switching, the increase in bias for full water splitting over 3 d was negligible (0.02 V; Figure 6).

The reversible bi-functional activity even extends to a commercially available iron foil (Alfa-Aesar; Puratronic; 99.995%). Fe foil proved to be bi-functionally active although with an inferior water splitting bias of ≈ 2.2 V at I = 10 mA cm⁻², likely due to the smooth morphology as compared to the nanostructured films prepared herein (Figure 1). Like the Fe film, its surface oxidizes at an anodic potential to form an active OER catalyst, which can be reduced back to the metallic HER catalyst under cathodic treatment. The foil, however, shows significantly lower stability for HER than the in-house prepared iron-only films (Figure 7a) with an increasingly negative potential over time, again due to either corrosion or passivation in the alkaline electrolyte solution. After only 12 h electrolysis with separate electrodes for HER and OER, the water splitting bias had increased by a further 0.2 V, whereas the bias of that with potential switching remained almost unchanged (Figure 7b).

The reversible potential-controlled interconversion of catalytically active HER and OER surfaces hence stabilizes the materials against a loss of activity. This feature can be used to extend the stability and operability time of iron-based materials with a bi-functional property since regeneration of the catalytic surface occurs every time the potential of the anode and cathode are reversed, without the need to halt water splitting.

2.4. Mechanism of Bi-Functional Activity and In Situ Electrochemical Regeneration

In agreement with the Pourbaix diagram for iron species in aqueous solution,^[49] metallic iron is likely to be present at sufficiently cathodic potential and is the likely site for HER catalysis. Likewise, at an anodic potential an iron(III) oxide will be present and is known to function as OER catalyst. **Figure 8** shows the proposed mechanism of the electrochemically reversible bi-functional activity of iron-only electrodes. Under sufficiently anodic bias, the material surface converts into an iron(III) oxide-(hydroxide), referred to as FeO_x which acts as catalyst for OER in the strongly alkaline solution. At a cathodic bias, surface sites are reduced to Fe(0), which is the active HER catalyst. Regardless of the initial identity of the iron-based material employed, the surface converts under bias into the species



Figure 7. a) *E*–*t* trace at a constant current density of -10 mA cm^{-2} for HER using iron-only films and a commercial Fe foil as working electrodes. b) *E*–*t* trace of an Fe foil (working electrode) at a constant current density alternating between +10 and -10 mA cm^{-2} every 30 min for 12 h (black trace). The red traces show the equivalent *E*–*t* traces without current alternation. In both cases, the aqueous electrolyte solution was 0.1 m KOH (pH 13) at room temperature and the counter and reference electrodes were Pt mesh and Ag/AgCl, respectively.

involved in this cycle, and thus shows very similar activity. In this study, Fe, FeO_x , and FeS_x were employed, but this is also likely to apply to other iron-based species.



Figure 8. Proposed mechanism of the electrochemical reversibility of bi-functional iron-only electrodes for water splitting in alkaline solution. An anodic potential generates the active FeO_x species for OER catalysis and a cathodic potential produces Fe(0) embedded in an iron oxide matrix as HER catalyst. Fe precursor represents the iron-based materials FeO_x , Fe, and FeS_x .

LSV and XPS were used to confirm this proposed mechanism of bi-functional activity. Figure S9 (Supporting Information) shows the cathodic LSV scans of FeO_x and FeS_x before and after cathodization at -10 mA cm⁻² for 12 h compared to an as-deposited Fe film electrode. In the case of FeO_x, the activation process clearly converts the active surface into a different catalytic species with almost identical activity to the asdeposited Fe film, strongly supporting a metallic iron species as the active sites for hydrogen evolution.

The model of potential-operated switch between Fe(0) (cathodic) and Fe(III) oxide (anodic) phases with concurrent switch from HER to OER catalysis has been further confirmed through XPS analysis of the electrodes after an HER step and after an OER step (Figure 9, and Figures S10 and S11 in the Supporting Information). The Fe2p XPS spectrum of an FeO_x electrode after 3 h HER activity shows the appearance of a new peak at 706.2 eV corresponding to Fe(0) (Figure 9).^[44] XRD of the same sample does not show the presence of crystalline features of α -Fe indicating that the oxide-derived Fe(0) catalyst is amorphous or a thin surface layer.^[29,50] Indeed, the oxide peaks fitted at 709.8 and 710.2 eV and their relative ratio confirm that the Fe(0) sites are held within an Fe(III) oxide matrix and this activated HER catalyst is very similar in surface composition to the as-prepared Fe film electrode (vide supra, Figure 2). The spectrum of FeO_x after 3 h OER activity is unchanged relative to the as-prepared material, indicating that FeO_x is itself the active oxygen evolving catalyst. Similarly, the Fe(0) peak seen in the Fe film after OER has decreased in relative magnitude (3.7%) to that before (5.6%), supporting increased iron oxide content in the OER active phase (Figure S11a, Supporting Information). The spectrum of the Fe film after HER is largely unchanged with only slightly increased iron content (5.9%), supporting iron(0) active sites in an oxide matrix as the hydrogen evolution catalyst.

 FeS_x was also found to be cathodically activated for HER (Figure S9, Supporting Information). The active HER catalyst could either be Fe(0) or indeed iron sulfide itself or a mixture of both species supported in an oxide matrix. The activation



Figure 9. XPS spectra (baseline corrected) of the $Fe2p_{3/2}$ region of asprepared FeO_x electrodes, after OER (3 h at +10 mA cm⁻²) and after HER (3 h at -10 mA cm⁻²). The solid (black) line shows the recorded trace and the dashed (blue) line represents the overall peak fit. Colored regions highlight the deconvoluted peaks.



process in each case would be the reduction of surface iron oxide or the reduction of oxidized sulfur (disulfide) sites to FeS respectively. No Fe(0) feature was observed for the FeS_{x} film after HER catalysis in the XPS spectrum (Figure S11b, Supporting Information). However, quantification of sulfur by both XPS and EDX indicates a loss of S during HER, suggesting that the active phase of the FeS_x film under HER is unstable to air after removal from the electrolyte solution and so could not be analyzed accurately by XPS. It is clear, however, that FeS_x converts into an FeO_x material at anodic potentials. The fitted Fe2p XPS spectrum of FeS_x after OER catalysis shows no Fe(II)-S peak at 707.8 eV and is almost identical to as-prepared FeO_x with iron(III) oxide peaks at 709.9 and 711.0 eV (Figure S11b, Supporting Information). Full loss of sulfur also occurs in the S2p spectrum (Figure S12, Supporting Information). This sulfide-derived FeO_x can then enter into the same potentialcontrolled Fe(0)–Fe(III) cycling of surface catalysts as the FeO_x and Fe electrodes.

The stabilization of the reported iron-only materials induced by potential switching is also explained by the potential-controlled interconversion of catalytically active surfaces between Fe and FeO_x. This occurs primarily by renewal of the Fe(0) catalytic HER surface upon cycling, which is subject to chemical corrosion by the aqueous solution and could also prevent overoxidation/dissolution of the iron oxide OER catalyst.

2.5. Iron-Only Electrodes in Water Electrolysis

Water splitting was performed with the iron-only electrodes (two-electrode configuration) as both anode and cathode in an alkaline electrolyzer with the electrochemical bias potential (*U*) recorded at a current density I = 10 mA cm⁻² (Figure 10). The films proved robust under rapid gas evolution and operated with a stable potential of ≈ 2 V. Analysis of the headspace gas of the electrolyzer using gas chromatography showed that, in all cases, the Faradaic efficiency for H₂ and O₂ evolution in the cathodic and anodic compartments respectively, was quantitative. For example, water electrolysis with an air-tight FeO_x/FeO_x cell at 10 mA cm⁻² resulted in the passage of a charge of 18 C after 30 min with the production of 98.1 µmol H₂ and 44.7 µmol O₂, which corresponds to a Faradaic efficiency of 105.2 ± 8.0% and 95.8 ± 8.8% for H₂ and O₂, respectively.

Figure 10 shows that the all-iron cells outperform an allplatinum analog, both in terms of cell bias and stability. A precious metal system comprising of a Pt cathode and RuO_x anode displays the highest activity with a bias potential of ≈ 1.56 V at I = 10 mA cm⁻², corresponding to a cell voltage efficiency of 95%.^[51] However, the all-iron equivalent competes strongly at 74% in the context of the superior abundance (at least eight orders of magnitude greater than any precious metal) and global availability.

2.6. Electrolysis of Seawater

Discussion of a global energy solution requires careful consideration of the economic and geographical availability of resources required for all components of the system. In this work so far,

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Figure 10. *E*-*t* trace for various electrolyzer cells (2-electrode 2-compartment setup) operating with a constant current density of 10 mA cm⁻² in a 0.1 \bowtie KOH (pH 13) aqueous electrolyte solution at room temperature. The cathode/anode pairs are indicated in the legend.

pure water has been used with 0.1 M KOH being added as electrolyte. However, in many cases it would be preferable to use seawater without the need for energy intensive and costly desalination, conserving the limited supply of fresh water.^[52] To this end, the water splitting ability of the iron-only cell was tested in an artificial seawater based electrolyte, where NaCl (0.6 M) was added to the KOH (0.1 M) solution. Headspace gas analysis (H₂ and O₂) after 30 min electrolysis of seawater revealed quantitative water splitting with the generation of H₂:O₂ in 2:1 (and no observable Cl₂ production as competing side-reaction). A charge of 18 C passed through the FeO_x/FeO_x cell over 30 min with the production of 99.6 μ mol H₂ and 53.6 μ mol O_2 , which corresponds to Faradaic efficiencies of $104.9 \pm 8.0\%$ and 106.6 ± 8.0%, respectively. Furthermore, the electrochemical response of FeO_x in LSV scans in an electrolyte solution containing NaCl remained unchanged at anodic potentials and no additional oxidative signals or a significant shift in the OER wave were observed (Figure S13, Supporting Information).

3. Conclusions

Readily scalable iron-only materials are bi-functional electrocatalysts for both water splitting half reactions in alkaline media with activity greater than previously reported bi-functional Co and Ni catalysts. This dual activity is caused by a facile interconversion of an oxide-supported Fe(0) phase active for HER under a cathodic bias into an iron oxide-hydroxide (FeO_x) phase active for OER under an anodic bias. This interconversion of catalytic species at the electrode surface is reversible and allows for regeneration of the catalytic surface upon switching of anode and cathode to enhance stability and lifetime of the electrolyzer system. In situ electrochemical regeneration through cycling of the applied potential with bi-functional electrodes is a novel concept to enhance the stability of a bi-functional electrocatalyst, which is otherwise limited by corrosion processes in aqueous solution. This approach can also help alleviate instability issues more generally associated with electrodes in

alkaline electrolyzers under conditions of fluctuating currents and gas pressures by regeneration of a bi-functional electrode and is particularly relevant in the context of intermittent renewable energy sources such as solar and wind. This strategy is specific to bi-functional materials that can catalyze both water splitting half reactions, as otherwise electrolysis would halt during potential cycling. Thus, our findings of an iron-based symmetrical water-splitting system with in-situ electrochemical regeneration represents a step toward the identification of economical, ultra-abundant water splitting catalysts for use in electrolysis and solar-to-fuel devices.

4. Experimental Section

Materials and Methods: Reagents used throughout this work were obtained from commercial suppliers and used as received. Laboratory grade reagents were used in all synthetic procedures and electrochemical grade reagents were used for analytical measurements. Millipore water (18.2 M Ω cm at 25 °C) was used throughout this work in both synthetic and electrochemical procedures. Solutions were made using analytical grade reagents and titrated to the desired pH, as determined by a pH electrode (Mettler Toledo; SevenEasy) using stock solutions of H₂SO₄ (Fisher Scientific Ltd.; > 95%) and KOH (Sigma-Aldrich; 99.99%).

Electrode Preparation: Briefly outlined below are the procedures used for synthesis and characterization of the thin film electrode materials. First, FTO coated glass (SnO₂/F; Sigma-Aldrich; 7 Ω sq⁻¹ sheet resistance) sheets $(300 \times 300 \times 2 \text{ mm}^3)$ were cut into $1 \times 3 \text{ cm}^2$ slides for use as conductive electrode substrates. Prior to film deposition, they were first cleaned by heating them in a solution containing hydrogen peroxide (H₂O₂; 100 vol.; Breckland Scientific Supplies), ammonia (NH₃; 35% solution, Fisher Scientific), and Millipore water in a ratio 1:1:5 at 80 °C for 2 h. The cleaned FTO substrates were rinsed with Millipore water and allowed to dry at room temperature. A 1×1 cm² area at each end of the slide was covered in a chemical- and heat-resistant epoxy tape (0.14 mm thick; 3M), leaving a central 1×1 cm² active electrode area for film deposition. The below depositions were optimized for highest-performance with the lowest loading of material. No comment is made as to the effect of thickness on stability or other properties of the materials.

Deposition of FeO_x Thin Films: Hydrated iron(III) oxide (FeOOH) was deposited onto the FTO substrate via CBD from an aqueous solution containing 0.15 M iron (III) chloride hexahydrate (FeCl₃·6H₂O; Sigma-Aldrich; \geq 99%) and 6.25 wt% urea (CON₂H₄; Breckland Scientific Supplies; 99%) at 90 °C for 1 h in a low-temperature furnace (Thermofisher Heratherm). Urea is thermally hydrolyzed in aqueous solution at 90 °C to produce in situ basic conditions, which causes the precipitation of iron oxide species from iron-containing solutions. Following CBD treatment, the electrodes were allowed to cool in situ before rinsing with Millipore water. The resultant yellow films were left to dry in air at room temperature. These films, designated as FeO_x, could be converted into various less hydrated iron(III) oxide phases by annealing under air at increasing temperatures in a furnace (Carbolite; ELF11/14B). Throughout this work, FeO_x refers to an annealing temperature of 200 °C for 30 min (2 °C min⁻¹ ramp rate).

Deposition of FeS_x Thin Films: Iron(II) sulfide was deposited onto the FTO substrate via a single-step CBD method from an aqueous solution containing 50×10^{-3} M iron(II) chloride tetrahydrate (FeCl₂·4H₂O; Sigma-Aldrich; 98%), 0.1 M thioacetamide (CSN₂H₄; Sigma-Aldrich; 98%), and 0.1 M urea at 90 °C for 6 h. Sulfide is released by thermal hydrolysis of thioacetamide, causing nucleation of iron sulfide onto the substrate. The resultant films, which were black with metallic sheen, were allowed to cool in situ before rinsing with deionized water and methanol, and dried in vacuo. They are designated as FeS_x.

Deposition of Fe Thin Films: Metallic iron was electrodeposited onto the FTO substrate using an adapted version of the conventional



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ferrous sulfate bath.^[43] Electrodeposition was effected from an aqueous solution containing 10×10^{-3} M iron (II) ammonium sulfate hexahydrate (FeSO₄(NH₄)₂SO₄·6H₂O; Sigma-Aldrich; 99%) as source of iron and 1 M ammonium sulfate ((NH₄)₂SO₄; Sigma-Aldrich; \geq 99.0%) as supporting electrolyte at room temperature. A current density of -10 mA cm⁻² was applied for 80 s. Coevolution of H₂ from the aqueous electrolyte solution happens rapidly once iron deposition has begun. The resultant electrode, designated Fe, was a metallic gray film. After deposition, the film was rinsed with Millipore water and methanol. For comparison, a pure metallic iron foil (Alfa-Aesar; Puratronic; 99.995%; 0.1 mm thickness) was also used as an electrode material.

Quantification of Fe Content: The amount of iron contained in each type of film was determined using UV-vis spectroscopy. Spectra were recorded on a UV-vis spectrophotometer (Varian Cary 50) in dual-beam absorbance mode. The spectra were background subtracted to exclude any absorbance from the solvent. Disposable plastic cuvettes (Fisher Scientific Ltd.; 10 mm path length) were used. The films were dissolved in concentrated hydrochloric acid (HCl; 20 mL; 11.65 M; Fisher Scientific) by submersion of the electrodes, followed by ultra-sonication for 2 h. The iron-containing species, [FeCl₆]³⁻ is formed under these conditions which has two strong absorptions in its UV-vis spectrum (Figure S14, Supporting Information) with λ_{max} at 362 nm (ε = 5756 M⁻¹ cm⁻¹) and 314 nm (ε = 5707 M⁻¹ cm⁻¹). These broad and intense LMCT bands obscure the expected low-intensity spin-forbidden d-d transitions. A calibration curve of the absorbance at 362 nm versus the concentration of [FeCl₆]³⁻ was made by taking the spectrum of HCl with regular additions of 0.5 \times 10⁻³ ${}_{M}$ solutions of FeCl₂·6H₂O and FeCl₃·6H₂O in HCl (Figure S14, Supporting Information). The same spectra and calibration is obtained using both Fe(II) and Fe(III) salts, confirming the universal applicability of this method to all iron-containing films, regardless of the initial oxidation state of iron, since in this concentration range, all Fe(II) is aerially oxidized to Fe(III) in conc. HCl. The average Fe content of each film type was determined using this method and the values are given in Table S1 (Supporting Information).

Deposition of Pt Thin Films: Metallic platinum was electrodeposited onto the FTO substrate using an aqueous solution containing 10×10^{-3} M potassium tetrachloroplatinate (II) (K₂PtCl₄; Precious Metals Online) as the source of platinum and 0.3 M sodium sulfate (Na₂SO₄; Sigma-Aldrich; \geq 99.0%) as supporting electrolyte at room temperature. The deposition was effected by running cyclic voltammetry from 0 to -1 V vs. Ag/AgCl/KCl(sat.) for two cycles at 200 mV s⁻¹ after purging of the solution with N₂ for 15 min. The resultant electrode, designated Pt, was a metallic gray film. After deposition, the film was rinsed with Millipore water and methanol. XRD, SEM, and LSV data for this Pt electrode are available in the Supporting Information (Figures S15–S17).

Deposition of RuO_x Thin Films: Hydrated ruthenium(IV) oxide was electrodeposited onto the FTO substrate using procedures adapted from the literature.^[53,54] An aqueous solution containing 5×10^{-3} M RuCl₃:xH₂O (Precious Metals Online) and 0.1 M KCl (Sigma-Aldrich; \geq 99.0%) and 10×10^{-3} M HCl as the supporting electrolyte at 50 °C was used. The deposition was effected by running cyclic voltammetry from -0.2 to 1 V versus Ag/AgCl/KCl(sat.) for 100 cycles at 50 mV s⁻¹. The resultant electrode, designated RuO_x, appeared as a brown film and was rinsed with Millipore water and methanol. RuO_x could be converted into various less hydrated ruthenium(IV) oxide phases by annealing under air at increasing temperatures. Throughout the remainder of this work RuO_x, a gray-black film, refers to an annealing temperature of 300 °C for 3 h (2 °C min⁻¹ ramp rate). XRD, SEM, and LSV data for this RuO_x electrode are available in the Supporting Information (Figures S15–S17).

Physical Characterization: The surface morphologies and thicknesses (Table S1, Supporting Information) of the various thin film electrodes were characterized using SEM (Phillips XL-30-SFGE). A freshly cut and untouched edge was used for cross-sectional views and elemental analysis was also undertaken at the same time using an Xsight light element EDX spectrometer (Phillips XL-30-SFGE). Phase analysis of the various thin films was carried out using XRD (X'Pert PRO, PANalytical BV). A slow scan rate of 0.5° min⁻¹ was used to resolve the peaks of

the thin film against the background of the crystalline FTO substrate. Structures were referenced against those registered in the International Crystal Structures Database (ICSD) using X'Pert HighScore software (PANalytical). XPS spectra were obtained at the National EPSRC XPS User's Service (NEXUS) at Newcastle University, UK, an EPSRC Mid-Range Facility. Analysis was performed using a K-Alpha (Thermo Scientific, East Grinstead, UK) spectrometer utilizing a monochromatic Al K α X-ray source (1486.6 eV, 400 µm spot size, 36 W). Survey spectra were collected with a pass energy of 200 eV and 3 sweeps, while high-resolution spectra were taken at 3 points on each sample surface to ensure consistency and charge neutralization was used throughout the analysis. Spectral analysis and peak fitting was carried out using CasaXPS software. The C1s (adventitious) peak was used as calibration standard.

Electrochemical Methods: All electrochemical measurements (voltammetric and transient) were taken at room temperature (20–25 °C) using an Ivium ComptactStat potentiostat (Ivium Technologies BV) controlled by IviumSoft software. Various thin film coated FTO-glass slides were prepared, as described above, and used as working electrodes. A fresh working electrode was used for each experiment. An aqueous Ag/AgCl/KCl(sat.) reference electrode (E(Ag/AgCl/KCl(sat.) = 0.197 V vs NHE) and a platinum mesh counter electrode were employed when required. The aqueous media contained either 0.1 м H₂SO₄ at pH 1, 0.1 м Na₂SO₄ (Sigma Aldrich; >99.0%) and triethanolamine (TEOA; Sigma-Aldrich; > 99.0%) at pH 7 or 0.1 M KOH at pH 13. Potentials are reported against the RHE using the Nernstian relation: E(V vs RHE) = E(V vs Ag/AgCl/KCl_{sat}) + 0.197 + (0.059 \times pH). Uncompensated cells resistance, or Ohmic drop, equal to *iR*, where *i* is the current flowing and R the cell resistance, was compensated for by inclusion into the potential calculation.

Electrical Impedance Spectroscopy (EIS) was used to determine the quantity *R* using the EIS function in the Ivium CompactStat. Impedance values were determined at the open circuit potential for each measurement. For the single compartment cell, the value of uncompensated resistance was typically in the range 20–30 Ω , whereas that in the larger two-compartment cell was in the range 80–120 Ω in the 0.1 \bowtie KOH electrolyte solution.

Electrochemical methods including LSV (1 mV s⁻¹ scan rate) and chronopotentiometry were carried out using a single-compartment cell and a conventional three-electrode setup. Reaction vessels were purged with inert gas, (N₂; BOC; 99.998%) for at least 15 min prior to experiments to remove atmospheric gases, namely O₂, which is potentially electroactive in the cathodic regime. Full water splitting electrolysis cells were run using a two-electrode setup with the cathode employed as the working electrode and the anode as the counterreference electrode. A two-compartment cell fitted with a Nafion 117 membrane was used to separate the headspaces of the cathodic and anodic compartments.

Product Quantification: The gaseous products (H₂ and O₂) were quantified by headspace gas analysis using a gas chromatograph (Agilent 7890A Series GC) with a 5 Å molecular sieve column (held at 45 °C) and a thermal conductivity detector. For H₂ and O₂ detection, N₂ and He were used as the carrier gas, respectively. The electrochemical cell was purged with 2% CH₄ in N₂ (BOC; 99.9995%; CH₄ is internal GC standard) for at least 15 min prior to experiment. \approx 20 µL aliquots of headspace gas were removed using a gas-tight syringe (Hamilton; GASTIGHT). Measurements were taken in triplicate and a minimum error of 8.0% was applied.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Additional data related to this publication is available at the University of Cambridge data repository (https://www.repository. cam.ac.uk/handle/1810/252751).



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