This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: S. Weiss, A. V. Radha, M. Ertl, C. McCammon and J. Breu, Mater. Adv., 2021, DOI: 10.1039/D1MA00381J.
Introduction

Resolving energy and environmental issues has been receiving enormous attention. It can be regarded as the critical challenge of the 21st century. Most of the proposed strategies focus on renewable energies to curb CO$_2$ emissions by gradually turning away from conventional fossil energy sources. Due to these energy sources’ intermittent nature, suitable storage methods are imperative to provide a continuous energy supply for grid management. For instance, energy can be stored in the form of chemical bonds, e.g., hydrogen. However, the bottleneck for green energy production, especially for grid management, is the low efficiency of hydrogen production. Unlike most of the chemical catalytic systems focus on expensive noble metals, a variety of transition metal oxides and hydroxides have been found to exhibit electrocatalytic activities in this half-reaction, called the Oxygen Evolution Reaction (OER).

For instance, energy can be stored in the form of chemical bonds, e.g., hydrogen. However, the bottleneck for green energy production, especially for grid management, is the low efficiency of hydrogen production. Unlike most of the chemical catalytic systems focus on expensive noble metals, a variety of transition metal oxides and hydroxides have been found to exhibit electrocatalytic activities in this half-reaction, called the Oxygen Evolution Reaction (OER).

Ideally, cheap and scalable anodes for OER are highly sought-after since noble metal oxides are considered unsuitable due to dissolution, high production price, and catalyst material maintenance. Being affordable and easy to manufacture, iron-based electrodes represent a viable option. Unfortunately, at OER operating conditions, the Pourbaix diagram of iron implies the dissolution of the electrode through the formation of ferrate (FeO$_4^{2-}$) anions. The dissolved ferrate is not stable in aqueous environments at pH 14 and will thus oxidize water to produce oxygen. Concomitantly with the reduction of the ferrate, undesirable corrosion products of iron are formed on the steel surface. The formation of this passivation layer may impede further corrosion but may also impair the performance of the electrode due to the low conductivity and/or lacking activity of formed products.

Using stainless steel, this uncontrolled rusting of the electrode can be mitigated. Among other transition metal additives, stainless steels typically contain at least 12 weight-% of chromium to reduce susceptibility to corrosion. Under ambient conditions, a thin chromium oxide layer passivates the surface. This, however, has been reported to contribute little or even reduce the OER activity of the stainless steel.

The Pourbaix diagram of Cr, moreover, indicates that the formation of CrO$_2^{2-}$ is thermodynamically favored under OER operating conditions. Indeed, previous studies have shown Cr leaching into the electrolyte in the long-term. The dissolution of chromium under sufficiently high anodic potentials has even been utilized to obtain thin Ni-Fe oxide layers representing a robust OER catalyst. However, Cr$^{VI}$ is known to be carcinogenic and must not be released into the environment but rather needs to be completely removed upon exchanging the
electrolyte.18, 19 Nevertheless, these and other13, 20, 21 studies clearly have proven the efficiency of oxidic layers on Fe-based substrates for OER catalysis. The steel types applied, however, often contain environmentally unfriendly or even toxic elements like Co, Cr, and Ni while processing often is time-consuming and requires harsh conditions.

Layered double hydroxides (LDHs) are regarded as one of the most promising classes of OER catalysts22 owing to the fact that they exhibit compositional flexibility and allow for tuning of the morphology. When optimizing the electrocatalytic properties, these features allow for optimization of electronic structures while providing high specific surface area at the same time.23 Generally, the composition of carbonate-LDHs can be described as $\text{M}^{2+}_{x}\text{M}^{2+}_{y}\text{(OH)}_z\text{(CO}_3^-)_{y/2}\cdot n\text{H}_2\text{O}$ with $0 \leq x \leq 2$. Previously, we have shown that the trivalent Fe-only layers, cations, and anions, and structural water.

Electrochemical characterization of the materials

All solutions used to synthesize the catalysts were prepared with Ar-saturated Milli-Q water (18.2 MΩ cm). Hydrogen peroxide solution (30 %) and ethanol absolute were supplied by VWR chemicals. Potassium hydroxide was ordered from Bernd Kraft GmbH and sodium bicarbonate from Grüssing GmbH. Substrates were prepared using custom cut steel plates (DC 01 – DIN EN 10130, Maschinenbau Feld GmbH). The nail varnish (shine last & go! gel nail polish; absolute pure) was bought from Cosnova GmbH.

Electrodeposition of GR and its conversion into GR*

Steel plates were cut to square-sized pieces of 1.4 cm length and any potentially pre-formed corrosion products were removed using grade P400 grinding paper and were further polished with 0.3 µm Al$_2$O$_3$ powder. Then they were cleaned by ultrasonication in ethanol for 5 minutes. Finally, each electrode was rinsed with water and ethanol to remove remaining loose metal particles and organic contaminants. Electrical contact was provided by using a PTFE-insulated Ag-wire and conductive silver adhesive. UV-curing glue was used to seal any exposed metal particles and organic contaminants. Electrical contact was provided by using a PTFE-insulated Ag-wire and conductive silver adhesive. UV-curing glue was used to seal any exposed silver. According to a previously published procedure,27 the plates were placed in a 0.4 M NaHCO$_3$ solution with the pH adjusted to 9.6 by dropwise addition of 10 M NaOH solution. Electrodeposition and electrooxidation were conducted using a CH-Instruments potentiostat 710E in a 3-electrode setup. A Fisher-type double net Pt/Ir electrode ($\varnothing$ 3 cm) and HydroFlex® hydrogen reference electrode from Gaskatel were used as a counter and reference electrodes, respectively. The plates were cyclically cycled from 0 to 0.2 V vs. RHE for 90 cycles with a scan speed of 10 mV s$^{-1}$. After completion, a greenish deposit was visible on the surface of the substrate. As a control experiment, the substrate was immersed in the given solution without any applied potential. Here, no formation of a deposit was observed after 12 weeks.

For complete oxidation of the mixed-valence GR to GR* two different methods were employed. For chemical oxidation, the sample was immersed in 40 mL of a 25 mM aqueous solution of H$_2$O$_2$. Electrochemical oxidation was achieved by simply increasing the voltage into the range 1.10 to 1.47 V vs. RHE (typically 5-10 cycles) subsequently to electrodeposition of GR. Scanning experiments were performed until no notable current was detectable. Both procedures yielded orange-brown deposits on the steel substrate plates and were then applied as anodes.

Figure 1 - Schematic comparison of the current-voltage curve for the OER of an unmodified, bare steel substrate (a) and the same substrate coated with the all-iron electrocatalyst GR* via a corrosion engineering process (b).

**Experimental**

**Materials**

To allow for quick measurements to minimize oxidation, powder X-ray diffraction (PXRD) traces for GR were collected on a Bragg-Brentano-type diffractometer (Empyrean) using a Ni-filtered Cu $K\alpha$ radiation source ($\lambda = 1.540598$ Å) equipped with a PIXcel detector. To further reduce fluorescence, PXRD patterns of air-stable GR*-samples were collected using a STOE STADI-P diffractometer with Ag $K\alpha_1$ radiation source.
(λ = 0.5594075 Å) in transmission geometry equipped with four MYTHEN2 R 1K detectors. The data collection was done in static mode for one hour, with samples loaded in 0.5 mm glass capillaries. However, to assist comparability, the diffraction traces acquired with Ag Kα1 radiation (Figure 2b) were recalculated assuming Cu Kα1 radiation. The infrared spectra of the powder samples were recorded using a JASCO Fourier transform infrared spectroscopy (FT-IR) 6100 spectrometer (400-4000 cm⁻¹ range, 1 cm⁻¹ resolution). Transmission electron microscopy (TEM) images were registered using a Zeiss / LEO EM922 Omega transmission electron microscope. Scanning electron microscopy (SEM) images were acquired using a Zeiss / LEO 1530 system. For Mössbauer spectroscopy, a small amount of powder was mixed with transparent nail varnish and spread over a region of 1 mm diameter on a plastic foil. The plate with hot melt adhesives. The obtained potentials were corrected by 85% of the uncompensated resistance (Equation 1). The ECSA was calculated by dividing Cdl by the specific capacitance C of a flat surface. A value of C = 0.04 mF cm⁻² was reported as an average value for different metal electrodes in an alkaline environment.34

$$\frac{1}{C} = \frac{(d\Delta j)/d\nu}{\Delta j} \quad (1)$$

Results and discussion
Various strategies have been employed to synthesize GR. These include Fe⁰/Fe¹ co-precipitation, oxidation of ferrous hydroxide,35 bacterial reduction of ferric compounds,36 and electrosynthesis.37 Formation of carbonate interlayered GR has been followed by Génin et al.38 by tracking the E₁ during the reaction.38 They further constructed the corresponding Pourbaix diagram, which identifies the stability field of GR with variation in pH and E.38 Based on previous investigations, a pH of 9.6 was considered most suitable to enable a successful deposition.37 For this pH, the E₁ range of GR can be identified to be located between 0 V and 0.15 V. For cyclic voltammetry, the window was chosen from 0 V to 0.2 V to account for possible overpotentials. After cycling, a greenish deposit was formed on the steel electrode. The intensity of the wave peak recorded during deposition increased steadily, suggesting a thickening of the deposited material layer with time (Figure S1). The obtained product was characterized utilizing XRD directly on the steel substrate to minimize unintended oxidation by air (Figure 2a).

$$\frac{1}{C} = \frac{(d\Delta j)/d\nu}{\Delta j} \quad (1)$$

The diffraction pattern of GR is in accordance with previous reports on the material (PDF #00-046-0098).39, 40 The d-spacing of 7.5 Å for the first reflection is characteristic for GR containing carbonate ions in the interlayer space and is usually assigned as the 003 plane of the 3R1 polymorph.34, 40 The coefficient of variation of the average of the basal spacing as calculated from individual 00l reflections was found to be small for GR (0.12%).

Electrochemical characterization
Electrochemical characterization was performed using an Autolab Potentiostat/Galvanostat PGSTAT204. Counter and reference electrodes were the same as used for the preparation of the material. If not noted otherwise, all electrocatalytic performance measurements were done in O₂-saturated 1 M KOH solution. The electrolyte for all measurements was purified using the cation-exchange resin Chelex® 100 (Bio-Rad Laboratories) following the procedure recommended by the producer.32 For electrochemical measurements, the exposed surface area was reduced to 1 cm² by sealing the rest of the plate with hot melt adhesives. The obtained potentials were corrected by 85% of the uncompensated resistance (iR) determined via current interrupt. Polarization curves were acquired by performing linear sweep voltammetry (LSV) in a range between 1.0 and 2.5 V with 5 mV s⁻¹. The overpotential η is given as the voltage potential difference to 1.23 V. Stability measurements were performed galvanostatically by applying a current of 10 mA, corresponding to a current density of 10 mA cm⁻², for 24 h. Galvanostatic stability experiments were carried out without iR compensation.

The determination of the electrochemical active surface area (ECSA) was conducted by performing cyclic voltammetry (CV) measurements in an Ar-saturated 1 M KOH at various scan rates (10, 20, 40, ..., 100 mV s⁻¹) in the potential window between 0.210 V and 0.310 V vs. RHE where there was no faradic current response. The double-layer capacitance (Cdl) was estimated by plotting Δj = j – j₀ at 0.260 V as a function of the scan rate ν (Equation 1).33

$$C_{dl} = \frac{0.5 \cdot (d\Delta j)/d\nu}{\Delta j} \quad (1)$$

Figure 2 - PXRD patterns of a) GR on a steel substrate as obtained through an electrochemical corrosion engineering process (*: substrate, #: partially oxidized product formed during measurement) and b) scraped off GR* powder as obtained through electrooxidation (GR* red) and chemical oxidation (GR* gray) of GR. Photographs of GR and GR* are shown as insets.

This journal is © The Royal Society of Chemistry 20xx
J. Name., 2013, 00, 1-3 | 3

Please do not adjust margins
This indicates little variance in the stacking distance of individual interlayers. As previously found, the remaining, weak in-plane reflections observed are in line with the 3R1 polymorph. A prominent reflection at 44.7° is caused by the underlying substrate and can be assigned to α-Fe(110) (PDF #00-006-0696).

Because of the oxygen sensitivity of GR, a controlled oxidation process is necessary to obtain phase pure GR*. Previously, we have shown that this can be achieved by subjecting GR to a H₂O₂ treatment as it allows for a rapid oxidation. Applying this chemical oxidation (GR*ChOx) to GR deposited on the steel electrode led to an immediate color change from green to orange-brown. Alternatively, the previously deposited GR on the steel substrate was subjected to electrochemical oxidation (GR*ElOx) via cyclic voltammetry in the range between 1.10 and 1.47 V vs. RHE. A similar color change to orange-brown was observed. A suitable potential range to facilitate the oxidation was identified using cyclic voltammetry over a broad range from 0.60 to 1.57 V (Figure 2b). Because both GR* samples are air-stable, the obtained products were scraped off the plate before being characterized using XRD (Figure 2b).

The powder XRD patterns of both GR* samples exhibit very few asymmetric and rather broad reflections. The featureless diffraction pattern is typical for GR*, 23, 39, 41 The diffraction pattern can be fully explained with a turbostratic disorder and concomitant interstratifications of domains with grafted and domains with intercalated carbonate. In any case, side phases are not indicated in the diffraction pattern. This is in contrast with reports, where GR was oxidized in ambient atmosphere or by bubbling oxygen through the suspension where mixtures of GR* with goethite are obtained instead of phase pure GR*. 27, 42 Both of the strategies presented herein, however, yield the desired product with no side phases. The first reflex of GR* appears at 7.1 Å (GR*ChOx) and 7.3 Å (GR*ElOx) and has been related to the basal spacing. 41 However, an integral 00l series is missing, indicating heavy random interstratification. The apparent basal spacing of both samples is lower as compared to the mixed-valence parent GR (7.5 Å). 40 In GR*ElOx the (002) reflection is rather sharp and more intense as compared to GR*ChOx. Moreover, even the (002) reflection (d = 3.7 Å) is visible while being submerged into the background when the oxidation is performed chemically.

We have previously shown that the oxidation of mixed-valence Fe-LDHs triggers partial grafting (i.e., chemical bonding) of interlayer carbonate to the brucite-like layers. 39 Density-functional theory (DFT) calculations have shown that the completely grafted structure shows a basal spacing, which is 0.3 Å smaller than for the non-grafted LDH. A similar trend was found in CoFe-LDHs, where it was found that a higher Fe-content promoted more grafting. In the presence of H₂O₂, the grafting was shown by DFT to proceed exothermically, which constitutes the driving force for the grafting process. 39 Grafting can also be qualitatively supported by FT-IR, as discussed below. Thus, the variations in the apparent basal spacings found for GR*ChOx and GR*ElOx are attributed to a random interstratification of grafted and intercalated domains. The higher intensity and higher d-value observed for GR*ElOx indicate significantly fewer grafted domains being produced by electrochemical oxidation as compared to chemical oxidation (GR*ChOx). Employing electrooxidation (i.e., in the absence of H₂O₂), the driving force for grafting might be smaller as compared to chemical oxidation and consequently, more intercalated (i.e. ungrafted) domains contribute to the random interstratification leading to an overall higher observed basal spacing of 7.3 Å.

To corroborate the varying grafting probability with the oxidation method, FT-IR spectra were recorded (Figure 3). Based on the symmetry of the carbonate ion, it is possible to experimentally distinguish between non-grafted interlayer carbonate, and carbonate ions that are grafted to the brucite layers. The former features a D₃h symmetry, whereas the latter shows symmetry reduction to C₃v. As shown in previous work, the ν₃ vibration band of CO₂ at 1350 cm⁻¹ may be used to quantify grafting. Symmetry reduction due to grafting manifests as an energetic splitting of this band to a second one observable at 1485 cm⁻¹, which is characteristic for the grafted carbonate species. 39 Irrespective of the oxidation method, these two bands are present. The relative intensity of these two bands furthermore allows for the assessment of the extent of grafted and non-grafted species qualitatively. Both bands, assigned to grafted and ungrafted carbonate species, exhibit roughly similar intensity for GR*ChOx. For GR*ElOx, however, the band's relative intensity at 1485 cm⁻¹ is notably decreased. Thus, it can be concluded that grafting of carbonate species is less prevalent when performing electrooxidation. This phenomenon is in line with the above interpretation of the XRD patterns (Figure 2b). It suggests that oxidation with a potent chemical oxidation agent, such as H₂O₂, provides a stronger driving force for grafting as compared to electrooxidation.

Aside from the basal reflections, only asymmetric, non-uniformly broadened reflections are observed in the diffraction patterns of both GR* samples. As previously shown they originate from two-dimensional diffraction by the brucite layers.
being stacked with random phase (turbostratic disorder) leading to hk-bands.

SEM images of both GR* samples (Figure S3a-d) confirm the coating on the substrate. Micrographs of the bare steel substrate merely show some surface roughness due to polishing (Figure S3e-f). For both the chemically and electrooxoxidized sample, the deposited layer features a plate-like morphology typically observed for LDHs. The steel substrate is completely coated and the coating appears uniform. The platy crystals of both GR* samples feature dimensions ranging from 0.4 µm to 4.5 µm in diameter and 40-80 nm in thickness. Large platelets are found to be intergrown, with smaller platelets providing an increased number of edges and corner sites, contributing to increased OER activity. The similar appearance of both samples indicates a topotactic transformation of GR to GR* and thus the morphology is determined already in the first step, the electrochemical deposition of GR, with little to no morphology change occurring upon formation of GR*.22 This conclusion is supported by SEM micrographs of GR acquired prior to oxidation (Figure S4).

Mössbauer spectra of chemically and electrooxoxidized samples are also very similar (Figure S5). The $^{57}$Fe spectra were acquired at room temperature consisting of a single, broad doublet with a mean quadrupole splitting of 0.67 mm s$^{-1}$ and 0.75 mm s$^{-1}$ and an isomer shift of 0.35 mm s$^{-1}$ and 0.36 mm s$^{-1}$ with respect to metallic iron. These values agree well with those expected for GR*.30,41 Complete oxidation from Fe$^{2+}$ to Fe$^{3+}$ can be concluded for both GR* catalysts as no residual ferrous doublet can be observed in the acquired spectra. Not surprisingly, Mössbauer spectroscopy is insensitive to the degree of grafting.

Both GR* samples were tested for OER catalysis. The electrochemical active surface area (ECSA) is calculated (Figure 4a) by performing CV in a non-faradaic regime at different scan rates (Figure S6). Due to the influence of the setup and method of determining the absolute ECSA,12 we only use the ECSA as an activity parameter to compare the samples obtained within this study. For this purpose, the relative ECSA of the untreated steel plate is compared with GR*$_{\text{ChOx}}$ and GR*$_{\text{ElOx}}$.

Compared to a non-coated sample, the controlled corrosion producing GR and then GR* leads to an approximately 2.4 and 2.7-fold increase in the ECSA for GR*$_{\text{ChOx}}$ and GR*$_{\text{ElOx}}$, respectively. Regarding the different oxidation methods, GR*$_{\text{ElOx}}$ has a slightly higher relative ECSA.

LSV experiments are performed and compared to the overpotential $\eta$ of the uncoated substrate (Figure 4b). Comparing the two GR* samples with varying degrees of grafting furthermore will allow for the first-time conclusions regarding the effect of grafting on the OER performance. GR*$_{\text{ChOx}}$ and GR*$_{\text{ElOx}}$ showed overpotentials of $\eta = 440$ mV and $\eta = 450$ mV, respectively, at a current density of 10 mA cm$^{-2}$ while for the uncoated, bare steel plate $\eta = 506$ mV is necessary. A current density of 100 mA cm$^{-2}$ was reached at overpotentials of 598 mV for GR*$_{\text{ChOx}}$ and 610 mV for GR*$_{\text{ElOx}}$. The absence of any notable pre-peaks is consistent with the expectations and conclusions from Mössbauer spectroscopy measurements, as both electrocatalysts have been fully oxidized to the all-ferric oxidation state.

Compared to the uncoated steel plate, both GR* catalyst materials show a clear OER activity improvement. The overpotentials at 10 mA cm$^{-2}$ are in the range reported for mòssbaurite synthesized at room temperature ($\eta = 540$ mV) and at a temperature of 50°C ($\eta = 400$ mV). The offset may be attributed to the different synthesis method and the rotating disc electrode setup being used to determine the latter values.

Despite the slightly higher ECSA of GR*$_{\text{ElOx}}$ compared to GR*$_{\text{ChOx}}$, the latter exhibits a higher activity over the probed potential range. Normalization of the polarization curves to the ECSA (Figure S7) further confirms the higher intrinsic activity of GR*$_{\text{ChOx}}$ compared to GR*$_{\text{ElOx}}$. We attribute this to the higher degree of carbonate grafting of GR*$_{\text{ChOx}}$ which can be regarded as a formal replacement of OH$^-$ with CO$_3^{2-}$, modulating the electronic structure and thus the redox activity of the metal center. According to the HSAB principle, the softer base OH$^-$ donates electron density to the adjacent metal centers more readily than the harder base CO$_3^{2-}$.45 Therefore, a lower electron density is expected at the electrocatalytically active transition-metal center for GR*$_{\text{ChOx}}$ as compared to GR*$_{\text{ElOx}}$. Investigations on NiFe-LDHs have shown that such reduced electron density, charge delocalization as well as the incorporation of electron withdrawing anions or cations can be beneficial for the facilitation of higher-valent electrophilic transition metal ion sites. At these sites, the nucleophilic attack of hydroxyl and water molecules is promoted, leading to an improved adsorption of reaction intermediates during OER.46,47

In order to investigate the stability and versatility of the catalyst during continuous operation, chronopotentiometry experiments were conducted. Here, the galvanostatic performance was investigated by applying a current corresponding to a current density of 10 mA cm$^{-2}$ for 24 h in 1 M KOH (Figure S8). Over this time, the necessary overpotential to maintain this current was recorded. Initially, GR*$_{\text{ElOx}}$ and GR*$_{\text{ChOx}}$ allow achieving the current density of 10 mA cm$^{-2}$ at lower potentials than the uncoated substrate. Throughout the experiment, an increase of the potential was recorded for...
GR\textsuperscript{+} \textsubscript{Eox} (+21 mV), GR\textsuperscript{+} \textsubscript{Eox} (+30 mV), and the uncoated bare steel substrate (+26 mV).

The decrease in performance of both GR\* samples may be related to various effects such as the physical detachment of catalyst material under operating conditions or degradation resulting in a loss of activity and active sites.\textsuperscript{23} Interestingly, the potential of GR\textsuperscript{+} \textsubscript{Eox} increased the most during the first 2 hours of the experiment (Inset Figure S8). Most likely, this is caused by the energy released during harsh chemical oxidation, which might result in a less intimate contact between the substrate and the catalyst. Thus GR\textsuperscript{+} \textsubscript{Eox} is more prone to a loss of electrical contact during operation. Due to the prior electrochemical treatment, GR\textsuperscript{+} \textsubscript{Eox} shows an initial performance increase which could be connected to an easier formation of percolation paths and active sites. In GR\textsuperscript{+} \textsubscript{Eox}, these improving changes are delayed and masked by possible detrimental alterations discussed earlier.

As expected, the performance of the uncoated steel also decreases, likely due to the formation of inactive corrosion products blocking the access to more electroactive centres. The formation of such products was also evidenced by brownish-black staining of the surface after the experiment.

To gain insight into the alteration of catalysts during the catalysis, post-catalysis SEM studies of the employed electrodes were performed. For the bare steel substrate, the results evidence the formation of a porous surface layer (Figure S9a-b). This indicates the oxidation of Fe\textsuperscript{0} to soluble Fe-species as predicted by the Pourbaix diagram discussed earlier. Alteration of the electrode under current load was also evident by the previously observed brown-black staining. Post-catalysis XRD measurements (Figure S10) indicate the presence of Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} deposits formed via reprecipitation. Presumably, these deposits are responsible for the deterioration of catalytic performance during chronopotentiometry measurements.

For GR\textsuperscript{+} \textsubscript{Eox} and GR\textsuperscript{+} \textsubscript{Eox} catalysts, the platelet-like morphology was generally preserved, although a loss of catalyst material (-23 %; determined gravimetrically) was observed during the stability experiment. SEM analysis moreover indicates a degradation of the hexagonal platelet shapes to more rounded corners and secondary deposits covering the platelets after 24 h (Figure S9c-f). Based on our previous study examining the stability of mössbauerite in a setup using a rotating disc electrode, we conclude that during electrolysis, small amounts of the catalyst can be dissolved into the electrolyte and are redeposited as amorphous iron (oxy)hydroxides.\textsuperscript{23} Post-catalysis XRD measurements (Figure S10) do not show any crystalline phase other than GR\* and steel.

Conclusions

Manufacturing catalyst-coated electrodes through a controlled, cheap, and time-efficient corrosion engineering process of steel presents a viable way to obtain electrodes for the oxygen evolution reaction. A carbon steel substrate was used to deposit the known iron-only electrocatalyst GR\* via its precursor GR. Clearly, the choice of oxidation method, i.e., chemically or electrochemically, has a notable influence on the catalyst’s structural constitution and performance. Chemical oxidation gives a higher degree of grafting, which appears to be advantageous for the catalytic performance.

Based on these results, further developments will aim towards maximizing the catalyst’s coverable surface area, e.g., by deposition on steel wool or iron foam. Of course, concomitant doping can further improve the performance as well.

Author Contributions

Sebastian Weiß: Investigation, Formal Analysis, Writing - original draft, Writing - review & editing; A.V. Radha: Investigation, Catherine McCammon: Investigation, Formal Analysis, Resources; Michael Ertl: Investigation, Josef Breu: Resources, Supervision, Writing - original draft, Writing - review & editing.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

The authors are grateful for financial support by the Deutsche Forschungsgemeinschaft (DFG) within the collaborative research center 840 “From particulate Nanosystems to Mesotechnology” (79971943; SFB 840). We thank Mirijam Zobel for the measurement time with her powder X-ray diffractometer. The authors thank O. Khoruszhenko for the graphic design. We further thank R. Timmins and C. Habel for advice and proofreading the manuscript. We appreciate the support of the Keylab for Optical and Electron Microscopy of the Bavarian Polymer Institute (BPI). We thank Marco Schwarzmann for the corresponding measurements. S.W. acknowledges the support from the Elite Network of Bavaria and thanks the graduate school of the Bavarian Center for Battery Technology (BayBatt) for ongoing support.

Notes and references

1. Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, Science, 2017, 355, eaad4998.
2. S. Chu and A. Majumdar, Nature, 2012, 488, 294-303.
3. J. Yin, A. Molini and A. Porporato, Nature Communications, 2020, 11, 4781.
4. D. Zhao, Y. Pi, Q. Shao, Y. Feng, Y. Zhang and X. Huang, ACS Nano, 2018, 12, 6245-6251.
5. I. Roger, M. A. Shipman and M. D. Symes, Nature Reviews Chemistry, 2017, 1, 0003.
6. L. Wu, L. Yu, X. Xiao, F. Zhang, S. Song, S. Chen and Z. Ren, Research, 2020, 2020, 17.
7. R. Tolouei, J. Harrison, C. Paternoster, S. Turgeon, P. Chevallier and D. Mantovani, Physical Chemistry Chemical Physics, 2016, 18, 19637-19646.
8. D. G. Lee and H. Gai, *Canadian Journal of Chemistry*, 1993, **71**, 1394-1400.
9. J. M. Schreyer and L. T. Ockerman, *Analytical Chemistry*, 1951, **23**, 1312-1314.
10. R. M. Cornel and U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, Wiley, 2006.
11. S. Papavinasam, in *Corrosion Control in the Oil and Gas Industry*, ed. S. Papavinasam, Gulf Professional Publishing, Boston, 2014, pp. 133-177.
12. S. Anantharaj, S. R. Ede, K. Kartthic, S. Sam Sankar, K. Sangeetha, P. E. Kartthic and S. Kundu, *Energy & Environmental Science*, 2018, **11**, 744-771.
13. H. Zhong, J. Wang, F. Meng and X. Zhang, *Angewandte Chemie International Edition*, 2016, **55**, 9937-9941.
14. B. A. Marinho, R. O. Cristóvão, R. A. R. Boaventura and V. J. P. Vilar, *Environmental Science and Pollution Research*, 2019, **26**, 2203-2227.
15. F. Guo, Y. Wu, H. Chen, Y. Liu, L. Yang, X. Ai and X. Zou, *Energy & Environmental Science*, 2019, **12**, 684-692.
16. X. Liu, B. You and Y. Sun, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 4778-4784.
17. H. Schäfer, S. Sada, L. Walder, K. Kuepper, S. Dinklage, J. M. R. Génin, S. J. Mills, A. G. Christy, O. Guérin, A. J. Kuzmann, S. Mills and C. Ruby, *Energy & Environmental Science*, 2015, **8**, 2685-2697.
18. H. Sun, J. Brocato and M. Costa, *Curr Environ Health Rep*, 2015, **2**, 295-303.
19. S. Mitra, A. Sarkar and S. Sen, *Nanotechnology for Environmental Engineering*, 2017, **2**, 11.
20. Y. Liu, X. Liang, L. Gu, Y. Zhang, G.-D. Li, X. Zou and J.-S. Chen, *Nature Communications*, 2018, **9**, 2609.
21. H. Schäfer, S. M. Beladé-Moussavi, L. Walder, J. M. R. Génin, S. J. Mills, A. G. Christy, O. Guérin, A. J. Kuzmann, S. Mills and C. Ruby, *Chemical Reviews*, 2014, **114**, 25157-25165.
22. Y. Wang, D. Yan, S. El Hankari, Y. Zou and S. Wang, *Advanced Science*, 2018, **5**, 1800064.
23. M. Ertl, C. Andronescu, J. Moir, M. Zobel, F. E. Wagner, S. Barwe, G. Ozin, W. Schuhmann and J. Breu, *Chemistry – A European Journal*, 2018, **24**, 9004-9008.
24. M. Usman, J. M. Byrne, A. Chaudhary, S. Orsetti, K. Hanna, C. Ruby, A. Kappler and S. B. Haderlein, *Chemical Reviews*, 2018, **118**, 3251-3304.
25. U. Schwertmann and H. Fechter, *Clay Minerals*, 1994, **29**, 87-92.
26. M. Abdelmoula, P. Refait, S. H. Drissi, J. P. Mihe and J. M. R. Génin, *Corrosion Science*, 1996, **38**, 623-633.
27. L. Legrand, L. Mazeronolles and A. Chausé, *Geochemical Cosmochimica Acta*, 2004, **68**, 3497-3507.
28. G. J. Long, T. Cranshaw and G. Longworth, *Mössbauer Effect Reference and Data Journal*, 1983, **6**, 22-49.
29. C. McCammon, V. Chaskar and G. Richards, *Measurement Science and Technology*, 1991, **2**, 657.
30. C. A. McCammon, *Hyperfine Interactions*, 1994, **92**, 1235-1239.
31. C. Prescher, C. McCammon and L. Dubrovinsky, *Journal of Applied Crystallography*, 2012, **45**, 329-331.
32. Bio-Rad Laboratories, Chelex(R) 100 and Chelex 20 Chelating Ion Exchange Resin - Instruction Manual, https://www.bio-rad.com/webroot/web/pdf/lsr/literature/LIT200.pdf, 2021.
33. H. Deng, C. Zhang, Y. Xie, T. Tumlin, L. Giri, S. P. Karna and J. Lin, *Journal of Materials Chemistry A*, 2016, **4**, 6824-6830.
34. C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *Journal of the American Chemical Society*, 2013, **135**, 16977-16987.
35. P. Refait and J.-M. Génin, *Corrosion science*, 1993, **34**, 797-819.
36. G. Ona-Nguema, M. Abdelmoula, F. J. Jorand, O. Benali, A. Génin, J. C. Block and J. M. R. Génin, *Hyperfine Interactions*, 2002, **139**, 231-237.
37. L. Legrand, S. Savoye, A. Chausse and R. Messina, *Electrochimica Acta*, 2000, **46**, 111-117.
38. J.-M. R. Génin, C. Ruby, A. Génin and P. Refait, *Comptes Rendus Geoscience*, 2006, **338**, 433-446.
39. P. Lyu, M. Ertl, C. J. Heard, L. Grajcar, A. V. Radha, T. Martin, J. Breu and P. Nachtigall, *The Journal of Physical Chemistry C*, 2019, **123**, 25157-25165.
40. J. M. R. Génin, A. Christy, E. Kuzmann, S. Mills and C. Ruby, *Hyperfine Interactions*, 2014, **226**, 459-482.
41. J. M. R. Génin, S. J. Mills, A. G. Christy, O. Guérin, A. J. Herbillon, E. Kuzmann, G. Ona-Nguema, C. Ruby and C. Upadhyay, *Mineralogical Magazine*, 2014, **78**, 447-465.
42. C. Ruby, M. Abdelmoula, S. Naille, A. Renard, V. Khare, G. Ona-Nguema, G. Morin and J.-M. R. Génin, *Geochemistry and Cosmochimica Acta*, 2010, **74**, 953-966.