Mechanistic insights into lepidocrocite conversion to hematite from variable temperature Raman microscopy

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Abstract

The consistent fabrication of high performance $\alpha$-$Fe_2O_3$ photoanodes for the oxygen evolution reaction remains a challenge. We work towards resolving this issue by developing in situ variable temperature Raman spectroscopy as a means to better understand the formation of $\alpha$-$Fe_2O_3$, using the conversion of $\gamma$-$FeOOH$ to $\alpha$-$Fe_2O_3$ under varied gaseous environments as a model case. The sensitivity of Raman spectroscopy to structural changes provides mechanistic insights that are not readily available in more conventional approaches, such as thermal gravimetric analysis and differential scanning calorimetry. The Raman spectra are combined with conventional thermal analyses to interpret the photoelectrocatalytic performance of a series of $\alpha$-$Fe_2O_3$ photoanodes prepared by systematic variation of a three-stage annealing protocol. The combined results suggest that protohematite, a form of $\alpha$-$Fe_2O_3$ where trapped hydroxyl ligands are balanced by Fe(III) vacancies, forms between 200 °C and 400 °C in a reaction environment-dependent fashion. This protohematite is shown to be remarkably persistent once formed, degrading photoelectrocatalytic performance. This research advances understanding of the $\gamma$-$FeOOH$ to $\alpha$-$Fe_2O_3$ structural transformation, illustrates a powerful method to study solid state phase transitions, and provides guidance for the synthesis of high quality $\alpha$-$Fe_2O_3$ from a convenient precursor.

1. Introduction

Heterogeneous electrocatalysis and photoelectrocatalysis are at the center of modern efforts to increase the sustainability of industrial fields ranging from energy storage [1, 2], to waste water treatment [3, 4], to the synthesis of fine chemicals [5, 6]. Much effort is focused on the identification of structural features or reaction sites that are either beneficial or harmful to catalytic performance; this information may lead to the ability to strategically maximize the number of beneficial features, or minimize the number of harmful ones. This presents a distinct challenge, however, because the rate limiting step in heterogeneous electrocatalytic reactions are generally minor equilibria that are believed to take place at a minority of sites on the solid-state surface [7, 8], and any structural defect risks shutting down photoelectrocatalysis on semiconductor surfaces [9–11]. Techniques that facilitate the identification, quantification, and removal or circumvention of specific structural features or defects are critical in advancing research in the field.

Being earth-abundant, low cost and the most thermodynamically stable phase of iron oxides, hematite ($\alpha$-$Fe_2O_3$) is widely studied for catalysis [12, 13], electrocatalysis [14, 15] and photoelectrocatalysis [16–19]. A multitude of techniques have been employed to synthesize hematite, including the thermal treatment of other iron oxide phases such as lepidocrocite ($\gamma$-$FeOOH$) [20, 21], goethite ($\alpha$-$FeOOH$) [22, 23], magnetite ($Fe_3O_4$) [24, 25] and akageneite ($\beta$-$FeOOH$) [26, 27]. The precursor selected, the atmosphere used, and the thermal treatment protocol influence the structural quality and properties of the $\alpha$-$Fe_2O_3$ product [26, 28, 29], including the performance towards photoelectrocatalytic oxygen evolution reaction (OER). It has further been shown that the kinetics for processes on the surface of iron oxides are altered by exposure to...
alkali cation solutions [30]. Variability in the structure of α-Fe₂O₃ is sufficiently high to introduce major inconsistencies in reported photoelectrocatalytic OER performance metrics and physical properties for α-Fe₂O₃ [19, 25, 31]. These metrics are sensitive to the quality of the bulk structure, electron transport properties, and the surface structure. Research efforts have, for example, demonstrated that oxygen vacancies in α-Fe₂O₃ can have a beneficial effect on photoelectrocatalytic OER [32–34], identified phase segregation in doped α-Fe₂O₃ that improves photoanode performance [35–37], revealed the detrimental influence of iron vacancies [29], and elucidated the role of surface states at the hematite–electrolyte interface [38, 39]. Establishing a detailed understanding of the nature of any potential structural defects, whether in the bulk or on the surface, and their effect on photoelectrocatalytic behavior, would provide a means to rationally optimize synthetic protocols. From a different perspective, which we are particularly interested in, the sensitivity of photoelectrochemical (PEC) performance of α-Fe₂O₃ to minute structural variations provides a useful measure of structural quality that can be correlated to spectroscopic results to acquire high quality structural information.

We demonstrated in previous work that the environmental conditions and heating protocol utilized to convert γ-FeOOH to α-Fe₂O₃ have significant impact on both structure and photoelectrocatalytic behavior [29]. The correlation of features within Raman spectra from α-Fe₂O₃ films with the band edge positions, photoelectrocatalytic onset and overall performance as a photoanode for OER were proposed to be caused by the trapping of protons and associated creation of Fe(III) vacancies within the bulk lattice. These defects persisted to 800 °C, the maximum temperature examined. Electrodeposition provides a facile, accessible means to fabricate uniform thin films of γ-FeOOH, making it a common starting point for α-Fe₂O₃ synthesis for photoelectrocatalysis [9, 40, 41]. Lepidocrocite is different from other iron oxides in that it passes through an intermediate phase, maghemite (γ-Fe₂O₃), before being converted to hematite [21, 27, 42, 43]. Double-chain edge-sharing Fe₃O(OH)₆ octahedra running parallel to crystal c-axis are the characteristic structure for γ-FeOOH, with edge-sharing motifs linking the chains to form two-dimensional layers that are hydrogen-bonded to each other [43, 44]. The intermediate γ-Fe₂O₃ phase presents a spinel structure similar to that of Fe₃O₄, but with exclusively Fe(III) the material becomes a defective spinel with cation vacancies in the octahedral sites [27]. Hematite has the corundum type crystal structure in hexagonally close packing, where Fe(III) occupies two-thirds of the octahedral sites [27]. The phase transformation from γ-FeOOH to α-Fe₂O₃ has been investigated by a range of techniques, including x-ray diffraction [21], electron paramagnetic resonance spectra [45], differential scanning calorimetry (DSC) and thermal gravimetric analysis [46], and in situ infrared spectroscopy [44]. The classic mechanism for this reaction is viewed as starting from a hydrated form of γ-FeOOH and proceeding via a two-step process, with a dehydration reaction at ca. 140 °C followed by dehydroxylation to γ-Fe₂O₃ at ca. 260 °C and conversion to α-Fe₂O₃ at ca. 500 °C [24, 27, 42, 47, 48]. The reported temperatures for each phase transition vary depending on the technique employed, the nature of the precursors, and the heating protocol. The particle morphology and size of lepidocrocite, for example, have been shown to influence the transition temperatures from γ-Fe₂O₃ to α-Fe₂O₃ [47, 49], but have little influence on transition of γ-FeOOH to γ-Fe₂O₃ [47]. Recent in situ Fourier-transform infrared spectroscopy (FTIR) studies combined FTIR-temperature programmed desorption (TPD) indicate a mechanism that is more intricate than the classical one, with the possibility of multiple reaction paths [44]. Resolution of vibrational bands for bulk OH and surface Fe-OH, Fe-µ-OH and Fe-µ₃-OH species in γ-FeOOH enabled the authors to show that ca. 50% of monodentate hydroxyl ligands at the surface are preferentially lost between 50 °C and 120 °C, after which all hydroxyl ligands are removed between 254 °C and 266 °C. TPD results confirmed H₂O release ca. 20 °C above the temperature where the bulk OH vibrations were removed [44]. The authors proposed the creation of vacant anion sites at the surface was necessary for the phase transition to proceed, that creation of these vacancies could be facilitated by H-bonding, but that hydroxide migration or water adsorption could fill these vacancies and result in persistence of hydroxyl groups in material. They further showed that simultaneous conversion of γ-FeOOH to γ-Fe₂O₃ and α-Fe₂O₃ is possible, rather than the traditional linear series of reactions [44]. It is clear that there remains much to learn regarding the structural evolution of iron oxides upon heating, and on developing more direct paths to the synthesis of high quality α-Fe₂O₃ through simple and accessible processes.

Herein, we perform in situ variable temperature Raman spectroscopy under varied atmospheres for the first time to study the mechanisms of thermally induced conversion of γ-FeOOH to α-Fe₂O₃. We track the growth and decay of all phases between room temperature and 800 °C under inert or oxidizing conditions, with or without humidification. Curve fitting of each series of spectra enables analysis of peak location, width and size as a function of temperature and environment. We compare this information to that obtained via the more traditional DSC and thermal gravimetric analysis. The combined results are used to interpret the observed photoelectrocatalytic behavior of a series of α-Fe₂O₃ photoanodes fabricated by a systematically varied three-stage annealing protocol.
2. Experimental

2.1. Lepidocrocite fabrication

Powder γ-FeOOH for variable temperature Raman microscopy studies were fabricated by oxidation of ferrous chloride tetrahydrate (ACS reagent grade, Alfa Aesar) [50]. The experiment was carried out in an ice bath to maintain a temperature of 5 °C. A total of 10.00 g of FeCl₂·6H₂O was dissolved in 200 ml of Milli-Q H₂O (18.2 MΩ) that was acidified with a few drops of 1 M H₂SO₄. The pH of the solution was increased to 6.5 by addition of 1 M KOH, then the solution was purged with air while adding 1 M KOH to maintain the pH at 6.5. When solution pH was stabilized at 6.5, the temperature was increased to 45 °C to complete oxidation of Fe(II) to Fe(III). The suspension was then cooled to room temperature and an orange powder was collected by vacuum filtration and dried in a furnace at 105 °C.

2.2. Photoanode fabrication

Lepidocrocite thin films were electrodeposited on fluorine-doped tin oxide coated aluminum borosilicate (FTO/ABS) glass (Solaronix S.A.) and subsequently annealed to convert them to hematite. Previous reports using this approach indicate film thicknesses to be 500–1000 nm [50]. FTO/ABS glass substrates were cleaned by ultrasonication using detergent solution, Milli-Q water (18.2 MΩ) and isopropanol. Then the glasses were dried by compressed air and put in a UV-irradiation chamber (GHO18T5VH lamp, Atlantic Ultraviolet). Thin film γ-FeOOH samples were prepared by purging a solution containing 0.02 M ferrous chloride tetrahydrate (ACS reagent grade, Alfa Aesar) and 1 M ammonium chloride with N₂ for 30 min. A 0.1 M KOH (>85%, Sigma-Aldrich) solution was then added to adjust pH to 7.0. A freshly cleaned FTO/ABS electrode was then held at 0.0 V vs Ag/AgCl (sat’d KCl) for 7 min at room temperature. A series of 16 photoanodes were prepared by systematically varying a three-stage annealing protocol from such γ-FeOOH films as a starting point. The annealing process was initiated by holding each electrode at 210 °C for 2 h under either N₂ or O₂. The environment was then changed to one of the four used in this study and the temperature increased to 550 °C and held for 2 h. The environment was then changed to either N₂ or O₂ for the final stage of annealing, where electrodes were held at 800 °C for 1 h. The thin film annealed at 350 °C, 600 °C and 800 °C and used in Raman mapping was prepared using a solution containing 0.02 M ferrous ammonium sulfate hexahydrate (ACS reagent grade, Fisher Chemicals) and 3 M ammonium chloride (ACS reagent grade, EMD Chemicals Inc.).

2.3. Raman spectroscopy

Measurements were carried out on a Renishaw inVia Reflex system equipped with a temperature-controlled stage (CCR1000, Linkam Scientific) using 532 nm (Renishaw DPSSL laser, 50 mW) laser excitation. Laser power was decreased to 5% for all measurements. Variable temperature Raman microscopy measurements on γ-FeOOH powders used a linear 4 °C min⁻¹ ramp from room temperature to 800 °C, with Raman spectra acquired every 2 °C (30 s). Experiments were duplicated to confirm the accuracy of the results. Measurements were repeated under four different gaseous conditions (N₂, O₂, N₂ + H₂O, O₂ + H₂O). The gas flow rate was maintained at 20 ml min⁻¹ using a mass flow controller (Masterflex Proportional Flow Controller, Cole-Parmer) and humidification was achieved by bubbling the purge gas through a room temperature H₂O reservoir before entry to the heat stage. Raman spectra were acquired and processed using Renishaw WiRE 5.2 software.

2.4. Thermal analysis

DSC and thermal gravity analysis (TGA) were simultaneously performed using a NETZSCH STA 409PC Luxx. A constant argon purge was maintained during a linear heat ramp of 4 °C min⁻¹.

2.5. Photoelectrocatalysis

Photoelectrochemical measurements were carried out using a Bio-logic SP300 potentiostat and a Scientech A1 Lightline solar simulator equipped with an AM1.5G filter. FTO/ABS substrates coated with thin film samples were mounted in a custom-made polyethylene cell. The working electrode window contacted the 1.0 M KOH electrolyte solution and a silicone O-ring masked the active surface area to 1.54 cm². Uncompensated resistance values were measured immediately prior to each electrochemical measurement. Samples prepared at 600 °C and lower typically show 20 W resistance, while those at 800 °C show 30 W. Photoelectrocatalytic measurements utilized back-side illumination, a reversible hydrogen electrode (RHE; Gaskatel HydroFlex, Gaskatel GmbH, Germany) served as the reference electrode, and clean FTO glass as the counter electrode. Electrochemical impedance spectroscopy was measured at 100 mV step intervals from 0.5 V to 1.5 V vs RHE with am amplitude of 10 mV.
3. Results and discussion

Variable temperature Raman spectroscopy measurements demonstrate the sensitivity of the mechanism for conversion of \( \gamma \)-FeOOH to \( \alpha \)-Fe\(_2\)O\(_3\) to atmospheric conditions. Variable temperature Raman spectra show three distinct spectra for iron oxide under both dry (figure 1) and humid (figure S1 (available online at stacks.iop.org/JENERGY/3/044002/mmedia)) conditions. The average spectrum between 28 °C and 100 °C contains the series of peaks expected for \( \gamma \)-FeOOH (figure 2(A)), denoted here from lowest energy to highest as \( L_1-L_4 \) [51, 52]. The average spectrum between 220 °C and 320 °C contains weak peaks at \( ca. \) 350 \( (M_1) \) and 500 cm\(^{-1} \) \( (M_2) \) and one strong, broad peak at 670 cm\(^{-1} \) \( (M_3) \), indicative of \( \gamma \)-Fe\(_2\)O\(_3\). A subsequent transition to \( \alpha \)-Fe\(_2\)O\(_3\) is seen in the average spectrum between 500 °C and 600 °C, with peaks at \( ca. \) 220, 280, 390, 490 and 600 cm\(^{-1} \) labeled \( H_1 \) through \( H_5 \) [49, 51]. A total of seven Raman-active vibrations are expected for \( \alpha \)-Fe\(_2\)O\(_3\). These seven vibrations, and a formally symmetry-forbidden \( E_g \) peak observed at \( ca. \) 660 cm\(^{-1} \), are resolved upon cooling to room temperature (figure 2(B)). The symmetry forbidden peak arises due a structural distortion; this vibrational mode has been shown to grow upon Si-doping of hematite, resulting in improved PEC performance [53–56], or to grow when iron vacancies form, resulting in a decrease in PEC performance [29].

The known thermal phase transitions, where \( \gamma \)-FeOOH is reported to convert to \( \gamma \)-Fe\(_2\)O\(_3\) near 260 °C and to \( \alpha \)-Fe\(_2\)O\(_3\) near 500 °C [27], are present in the data acquired under all conditions (figures 1 and S1). Clear differences are observed, however, in the transition temperatures, the temperature-induced shifting of peak locations and the relative peak intensities.

Curve fitting of individual spectra enables the structural transitions observed under different environments to be compared to one another. A subset of peaks was selected for detailed analysis of individual spectra, with each selected to minimize peak overlap with other phases and ensure maximum signal-to-noise ratios by analyzing strong peaks. Selected peaks include \( L_1 \) and \( L_2 \) for \( \gamma \)-FeOOH, \( M_1 \) for \( \gamma \)-Fe\(_2\)O\(_3\) and \( H_1-H_3 \) for \( \alpha \)-Fe\(_2\)O\(_3\), shown in the sample spectra for the dry \( N_2 \) series in figure 2(A) and other conditions in figure S2. The changes in area of the remaining peaks for each phase are consistent with those of the selected peaks, but their weaker intensity lead to poor signal-noise (figure S3).

Changes in intensity and energy of the selected Raman vibrational modes indicate a more nuanced phase transition than is implied by the traditional two-step, lepidocrocite-maghemite-hematite, mechanism. Using the sample heated under dry \( N_2 \) as an example, a first stage of \( \gamma \)-FeOOH decay proceeds until \( ca. \) 110 °C and involves an approximately linear loss of peak intensities (figure 3(A)) and a red-shift in \( L_2 \) (figure 3(B)) with respect to temperature. The rate of intensity loss accelerates in a second stage to yield a clear peak at 160 °C in first derivative plots. This second stage is accompanied by an exponential red shift in \( L_2 \) peak location. The loss of intensity for lepidocrocite peaks is mirrored in both direct and derivative plots for \( M_3 \) growth, thereby confirming that this second stage involves conversion of lepidocrocite to maghemite. A blue shift in \( M_3 \) and an increase in peak intensity are observed until \( ca. \) 200 °C–210 °C, which is well-aligned with the complete loss of \( L_1 \). Notably, this lies \( ca. \) 50 °C lower than the phase transition temperature often reported by

![Figure 1](https://stacks.iop.org/JENERGY/3/044002/mmedia)
techniques such as TGA, DSC and TPD [21, 42, 43]. Maghemite has nonetheless been observed as low as 150 °C and obtained in phase-pure form as low as 225 °C, [46] both of which also lie below the typically reported phase transition temperature. After reaching a maximum in both intensity and peak location, $M_3$ decays in a three-stage process. The first stage of maghemite decay is seen as a sudden 8 cm$^{-1}$ red shift in $M_3$ location and a decay in intensity, which transitions into an approximately linear decrease in intensity and a red shift with respect to temperature. A third stage begins at ca. 370 °C, with a faster linear decay and a more extreme red shift. This third stage of $M_3$ loss is concomitant with first detected growth in $H_2$, with mirrored behavior in $M_3$ and $H_2$ peak intensities confirming the conversion of maghemite into hematite. The initial growth of $H_2$ reaches a plateau at ca. 520 °C that extends until ca. 575 °C, after which a second growth stage yields a first-derivative peak at 588 °C. The intensity of $H_2$ is then stable until 700 °C, after which it rapidly decays. This apparent decay is induced by decreased signal-to-noise caused by increased baseline signal from blackbody radiation. These in situ spectroscopic results suggest that there are at least two distinct steps within each of the two different structural transitions.

Differential thermal analysis results for γ-FeOOH under a dry argon environment are in agreement with previously reported behavior [42, 57], but provide a different perspective than the spectroscopic results. TGA traces show gradual mass loss from 80 °C to 200 °C, accelerating thereafter to produce a single peak at 242 °C in $dm/dT$ plots (figure 3(C)). The mass loss tails until ca. 575 °C, after which a second growth stage occurs. The theoretical mass loss of 10.1%, calculated assuming no physisorbed $H_2O$, is approached at 800 °C. A measured mass loss of 8.4% at 500 °C indicates that the synthetic hematite retains excess hydroxide, which can alternatively be viewed as iron vacancies (vide infra).

Simultaneously acquired DSC results produce numerous features (figure 3(D)):

(a) Exothermic peaks at 77 °C and 107 °C assigned to the loss of singly coordinated hydroxyl or aqua ligands, based on previous variable temperature FTIR and TPD studies [44]. The location of these peaks are aligned with the first stage of $L_1$ intensity loss. The removal of oxygen from lepidocrocite has been reported to involve proton transfer between adjacent hydroxyl sites to release $H_2O$ and leave a surface vacancy.

Figure 2. Sample Raman spectra acquired from a heat ramp under dry $N_2$ conditions. (A) Average spectra in the noted temperature regions and assigned to either γ-FeOOH, γ-Fe$_2$O$_3$ or α-Fe$_2$O$_3$. (B) Spectrum of α-Fe$_2$O$_3$ acquired upon completion of heat ramp and cooling to room temperature. Shaded peaks represent those used for further analysis of variable temperature Raman results.
Figure 3. Variable temperature Raman and thermal analysis of \( \gamma \)-FeOOH under dry, inert atmospheres. The (A) integrated peak area for major peaks in \( \gamma \)-FeOOH (\( L_1 \)), \( \gamma \)-Fe\(_2\)O\(_3\) (\( M_3 \)) and \( \alpha \)-Fe\(_2\)O\(_3\) (\( H_2 \)) and (B) the peak locations for \( L_2 \), \( M_3 \) and \( H_2 \). From left to right, curves are for \( L_1 \) (black), \( M_3 \) (red) and \( H_2 \) (blue). Data shown was acquired while heating under \( N_2 \). Simultaneously performed (C) thermogravimetric analysis and (D) differential scanning calorimetry under an argon environment.

\[ g \text{FeO(OH)} \rightarrow g \text{FeO}_{1-2x} \text{(OH)}_{1-2x}(□)_x + x \text{H}_2\text{O}. \]
An endothermic peak at 242 °C is aligned with the major mass loss event observed by TGA, with the pair of peaks being routinely assigned as direct conversion of lepidocrocite to maghemite [42, 58]. This feature is notably misaligned with $L_1$ loss, instead beginning at the temperature where $L_1$ is fully lost and $M_2$ is at maximum intensity and energy (figure 3). The DSC peak is then aligned with a rapid 8 cm$^{-1}$ red shift in $M_1$ and its sudden drop in intensity. The misalignment of major chemical processes observed via thermal and spectroscopic techniques provides evidence that the transition of lepidocrocite to maghemite occurs in two distinct steps. Magnetic studies have previously suggested that initial dehydroxylations of lepidocrocite between 150 °C and 200 °C yields an ordered but unstable form of maghemite, which decays to a more crystalline form of maghemite at 250 °C [47]. The temperature regime previously reported for this initial dehydroxylations reaction is perfectly aligned with the major transition observed here via Raman microscopy, and with a region of accelerated mass loss via TGA. We therefore assign the major transition observed in Raman spectroscopy to the formation of an initial, highly protonated form of maghemite as in equation (2). The sudden red shift in $M_2$, the endothermic DSC peak and the large mass loss must then be assigned to further dehydroxylations and crystallization of maghemite as in equation (3). These chemical equations are written from the perspective of the products containing iron vacancies rather than excess oxygen, as is conventional [22, 23, 59], and with variables for H$_2$O stoichiometry release rather than full fractional amounts. Total mass losses for these two stages are 1.98% and 8.67%, suggesting that $y = 1.26$ and $z = 0.27$ capture the maximum extent of the respective reactions.

$$2\gamma - \text{FeO}_1 + x(\text{OH})_1 - 2x(\square)x \rightarrow \gamma - \text{Fe}_2 - 3/2\text{O}_3 - y(\text{OH})_y + a\text{H}_2\text{O}. \quad (2)$$

$$\gamma - \text{Fe}_2 - 3/2\text{O}_3 - y(\text{OH})_y \rightarrow \gamma - \text{Fe}_2 - 3/2\text{O}_3 - z(\text{OH})_z + b\text{H}_2\text{O}. \quad (3)$$

A broad exotherm stretches from approximately 200 °C to 400 °C in the DSC trace. This feature has been previously assigned as an undefined structural rearrangement in hematite [42, 46], and is aligned with the second stage of intensity loss and a linear red shift in $M_1$. Raman microscopic mapping of samples heated at 350 °C reveal the Raman spectrum for hematite scattered across the surface (figures 4(A)–(C)), but comparison of these spectra with those acquired on samples synthesized at 800 °C show a 50-fold difference in intensity (figure 4(D)). These observations, and the fact that subsequent hematite formation is also exothermic, lead us to assign the broad exotherm to the DSC and the associated changes in Raman spectra to the formation of highly defective hematite. A loss of only 0.53% mass occurs between the end of the endothermic DSC peak at 265 °C and 400 °C. This step is therefore believed to yield a phase of hematite with residual hydroxide ions known as protohematite, which is conventionally represented as containing iron vacancies through the formula $\alpha$-Fe$_{2.85}$O$_3$–δ(OH)$_\delta$ [23, 59, 60]. This process overlaps with those assigned to reaction (3) in the DSC and Raman spectra, suggesting that equation (4) proceeds as a branching reaction path from reaction (2). Maintaining the approximated value of $y = 1.26$ through reaction (4) would yield an implausibly high iron vacancy concentration in $\alpha$-Fe$_{1.58}$O$_{1.74}$(OH)$_{1.26}$. The lowest crystallographically determined partial occupancy for iron sites in protohematite is 0.88 (i.e. $\alpha$-Fe$_{1.76}$O$_{2.64}$(OH)$_{0.72}$) [23, 59], but values of 0.917 ($\alpha$-Fe$_{1.85}$O$_{2.5}$(OH)$_{1.5}$) are more common [23, 61, 62]. Convolution of mass loss from the overlap of (2) and (4) complicates quantitative determination of stoichiometry, so equation (4) is written to yield the most commonly observed structure.

$$\gamma - \text{Fe}_2 - 3/2\text{O}_3 - y(\text{OH})_y \rightarrow \alpha - \text{Fe}_{1.83}\text{O}_{2.5}(\text{OH})_{0.5} + c\text{H}_2\text{O}. \quad (4)$$

A second exothermic process that produces a peak at 489 °C is assigned as equation (5), which is the conventionally reported formation of hematite that proceeds from equation (3) [24, 63]. This transition is aligned with the first major growth stage in $H_2$ and a linear red shift in its location. The DSC trace indicates that the transition is complete at ca. 580 °C, which aligns with the end of the plateau between the first and second stages of $H_2$ growth. A total mass loss of 8.67% at this temperature suggests that the average structure at this point can be represented as $\alpha$-Fe$_{1.91}$O$_{2.73}$(OH)$_{0.27}$, which is equivalent to the composition commonly reported for protohematite [23, 61, 62].

$$\gamma - \text{Fe}_2 - 3/2\text{O}_3 - z(\text{OH})_z \rightarrow \alpha - \text{Fe}_2\text{O}_3 + d\text{H}_2\text{O}. \quad (5)$$

The second stage of $H_2$ growth begins immediately after completion of this exothermic process, with a rapid increase in intensity paired to a 6 cm$^{-1}$ red shift. The DSC trace provides no measurable signals during this second process, but the TGA results do exhibit a gradual mass loss to yield a total 8.15% mass loss at 740 °C. This second event is assigned to the dehydration of protohematite as represented in equation (6) [62].
Figure 4. Raman microscopic map of lepidocrocite samples heated to 350 °C in a dry O₂ environment. (A) White light image and (B) a corresponding Raman spectral map where hematite peaks are observed. (C) The spectra averaged across the two 2 × 2 µm areas identified in panel A. (D) Comparison of the spectrum for hematite observed at 350 °C with spectra acquired for samples heated at 600 °C and 800 °C, with intensities scaled to enable comparison.

\[ a - Fe_{1.83}O_{2.5}(OH)_{0.5} \rightarrow \alpha - Fe_2O_3 + 0.27H_2O. \]  

A sharp endothermic peak appears in the DSC trace at 759 °C, which is coincident with a further 0.5% mass loss process in the TGA. The surface of hematite is known to release O₂(g) near 1000 K under oxygen deficient atmospheres to yield magnetite (Fe₃O₄), with the specific transition temperature dependent on O₂ partial pressure [64]. We therefore attribute these thermal features to a reaction on the hematite surface. No clear changes are observed to correspond with this process, but blackbody radiation from the reaction cell at these temperatures dramatically decreases the intensity of observed peaks due to a decrease in signal to noise.

If protohematite is represented as a singular composition, which the consistency in past crystallographic reports suggests to be valid [60, 62], the TGA results indicate that the net reaction at 580 °C under dry N₂ can be represented by equation (7), and that at 800 °C as equation (8)

\[ 2\gamma - FeO(OH) \rightarrow 0.49\alpha - Fe_2O_3 + 0.51\alpha - Fe_{1.83}O_{2.5}(OH)_{0.5} + 0.83H_2O. \]  

\[ 2\gamma - FeO(OH) \rightarrow 0.82\alpha - Fe_2O_3 + 0.18\alpha - Fe_{1.83}O_{2.5}(OH)_{0.5} + 0.94H_2O. \]  

Speciation plots showing the area of Raman peaks versus temperature confirm that the intensity loss and growth phases are observed in each reaction environment, albeit with the environments introducing differences (figure 5). The first stage of \( \gamma \)-FeOOH decay contributes 30%–50% of the overall lepidocrocite peak loss, depending on the gaseous environments. Derivative plots show the maximum rate of lepidocrocite loss to be in the second stage near 162 °C for three of the environments; the maximum rate of loss under
Figure 5. Speciation plots showing the normalized area of well-resolved peaks in spectra acquired during variable temperature Raman spectroscopy experiments. Data for γ-FeOOH (L₁, black), γ-Fe₃O₄ (M₁, red) and α-Fe₂O₃ (H₂, blue) is shown under (A) dry N₂, (B) humid N₂, (C) dry O₂ and (D) humid O₂.

Figure 6. Position of selected peaks in spectra acquired during variable temperature Raman spectroscopy experiments. Data is shown for strong peaks in (A) γ-FeOOH (L₁, black), (B) γ-Fe₃O₄ (M₁, red) and (C) α-Fe₂O₃ (H₂, blue) under dry N₂, humid N₂, dry O₂ and humid O₂ (listed from top to bottom).
Figure 7. Pairwise comparison of photoelectrocatalytic oxygen evolution performance of α-Fe₂O₃ films synthesized by a varied three-stage annealing protocol. Comparison of the role of O₂ versus N₂ in the intermediate 550 °C annealing step on photocurrents in (A) dry and (B) humid conditions. Comparison of the first derivative of photocurrents to demonstrate the influence of O₂ versus N₂ environments in the final 800 °C annealing step on the onset for photoelectrocatalysis under (C) dry and (D) humid conditions. Note that the 16 photoanodes analyzed are distributed across panels (A) and (B), and differently across panels (C) and (D).
N$_2$ in the second heating stage were compared directly to those using humid N$_2$ and to dry O$_2$. No influence can be confidently assigned for atmosphere variation during the first stage of annealing on photoelectrocatalytic OER performance. A pronounced effect appears during the second heating stage, however, where dry O$_2$ and humid N$_2$ environments induce poor PEC performance relative to dry N$_2$ and humid O$_2$, respectively (figures 7(A) and (B)). The primary difference in the 210°C–550°C temperature range for these two conditions is a more rapid 0.26% K$^{-1}$ rate of decay in $M_3$ intensity (figure 5). This stage of $M_3$ decay was noted above to align with the broad exothermic process in the DSC results (figure 3), which was assigned as the formation of protohematite through reaction (4). The more extreme slope therefore provides a signature of protohematite formation. The third annealing stage yields a trade-off in performance parameters, with N$_2$ yielding higher photoelectrocatalytic currents (figures 7(A) and (B)) and O$_2$ inducing a cathodic shift in the onset of photoelectrocatalytic OER (figures 7(C) and (D)). Annealing α-Fe$_2$O$_3$ under N$_2$ is known to introduce oxygen vacancies and reduce Fe(III) to Fe(II) [65, 66], which has been reported to improve PEC performance [33, 34, 66]. The root cause of this performance trade-off is revealed by Mott–Schottky analysis, which shows that the N$_2$ environment yields charge carrier densities between one and two orders of magnitude greater than those annealed under O$_2$ (table S1), but an O$_2$ environment shifts the flat band potential cathodically. This behavior reflects the balance that is known to exist between electron transfer kinetics at the solution interface and the photovoltage, which are influenced by changes in charge carrier density [32, 33]. Comparison of the PEC curves in figures 7(A) and (B) make it clear that the charge carrier density and flat band potential set by the final annealing environment do not override previous sample handling—samples treated at 550°C under humid N$_2$ or dry O$_2$ in the second heating stage perform poorly regardless of final heating stage. The variable temperature Raman experiments yield another fingerprint for these protohematite-forming conditions, with the decay of α-Fe$_2$O$_3$ Raman vibrations beginning near 600°C, which is 100°C lower than the conditions that yield better-performing photoanodes (figure 5). The iron vacancies introduced during protohematite formation at intermediate temperatures therefore persist to high temperatures and play a critical role in final PEC performance.

4. Conclusions

The influence of gaseous environments on the multi-step transition of γ-FeOOH to α-Fe$_2$O$_3$ was examined using in situ variable temperature Raman spectroscopy. The Raman spectra reveal that each of the traditionally reported reaction steps, namely γ-FeOOH to γ-Fe$_2$O$_3$ then γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$, are convoluted with an additional structural change. Comparison of variable temperature Raman results with TGA, DSC and photoelectrocatalytic OER data leads us to assign this additional process to the conversion of γ-FeOOH to protohematite (α-Fe$_{1.83}$O$_{2.5}$OH)$_{0.5}$, which occurs between 200°C and 400°C. Protohematite is subsequently converted into hematite above 500°C, but PEC results suggest that it cannot be quantitatively removed. The reaction environment present during initial formation of α-Fe$_2$O$_3$ is shown to influence the relative amount of protohematite formed, and fingerprints for the influence of this protohematite on structural evolution are found in the variable temperature Raman spectra. The known ability to increase photocurrents for OER by annealing at high temperatures under N$_2$ or lower photoelectrocatalytic onset by annealing under O$_2$ are confirmed. These treatments do not override the effects caused by protohematite formation, however, as a persistent degradation of photoelectrocatalytic performance is superimposed on these effects. Judging from PEC performance, the formation of protohematite is best minimized through use of a dry N$_2$ environment for the conversion of γ-FeOOH to α-Fe$_2$O$_3$.

Author contributions

The manuscript was written with contributions from all authors.

Data availability

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

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