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Nanoporous Fe₂O₃ and soluble Fe(II) intermediates accelerate the electrodeposition of Fe in NaOH(aq)

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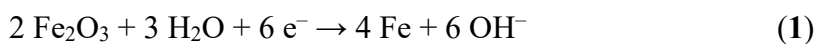
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Abstract:

Electrochemical conversion of iron oxide to iron metal can enable low-cost batteries for long duration energy storage and zero-emissions ironmaking for steel. Iron oxides such as hematite can be electrochemically reduced to metallic iron in concentrated alkaline electrolytes at modest temperatures, but the relative influence of solid-state and dissolved intermediates at practical reaction rates remains unclear. Here we prepare a homologous set of well-defined hematite particles to measure how the nanoscale morphology of oxides controls both their reactivity and apparent reduction mechanism in concentrated hydroxide. Correlated electron microscopy and rotating-ring-disk-electrode measurements revealed that nanoporous hematite and solid intermediates formed iron via a dissolution-redeposition pathway. In contrast, dense hematite particles directly formed iron metal via reactive fracture. While previous studies on iron electrowinning have primarily emphasized the role of particle diameter at the micron scale, these results demonstrate the importance of the dissolution-redeposition pathway to support rapid reaction rates and suggest that nanoscale porosity controls iron oxide reactivity at temperatures < 100 °C. Therefore, iron-oxide-to-metal electrolyzers and fast-charging iron-air batteries supported by curtailed electricity can increase the rate of metal formation by accelerating fracture and dissolution in reactant oxides.

Keywords: hematite, ironmaking, electrodeposition, porous materials, TEM, nanopores

Iron (Fe) metal is essential in modern society, and may soon play an important role in inexpensive, long duration energy storage systems.¹⁻³ Globally, the reduction of iron oxides to metal during primary steelmaking contributes ~7% of annual carbon dioxide emissions and potential decarbonized alternatives have yet to realize commercial operation.⁴⁻⁷ The majority of these sector-wide emissions occur during the chemical reduction of processed iron ores (largely hematite, α -Fe₂O₃) in blast furnaces, with coal-derived CO serving as the reductant and CO₂ produced as the oxidized product. These process CO₂ emissions can be avoided if Fe is reduced instead using zero-carbon electricity and water. For example, α -Fe₂O₃ can be directly reduced in water to form iron and hydroxide, OH⁻ (**Equation 1**).^{8,9}

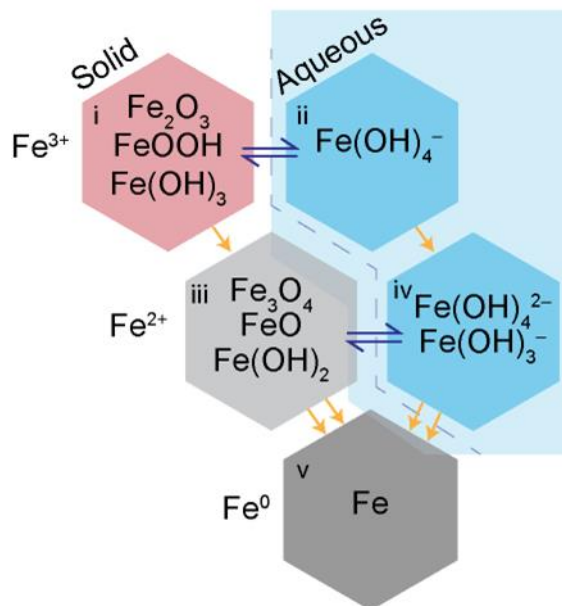


The reduction of H₂O to H₂ is a source of parasitic current as it is generally thermodynamically favorable compared to Fe formation. This reaction also occurs at the negative electrode of iron-air batteries, where controlling the selectivity between Fe and water reduction can limit the maximum charging rate.³

Pathways for reducing α -Fe₂O₃ to Fe can be classified as all-solid-state or dissolution-redeposition mechanisms, with the latter requiring the presence of at least one soluble (aqueous) intermediate (**Scheme 1 ii, iv**). Although α -Fe₂O₃ is only sparingly soluble in concentrated OH⁻ electrolytes, the solubility of ferrous and ferric species increases at the temperatures commonly used in electrodeposition experiments (80–110 °C).^{10,11} Trace quantities of dissolved intermediates play an important role in geochemical processes involving α -Fe₂O₃.^{12,13} Corrosion and redeposition of Fe in 20 M NaOH at 80–120 °C has been shown to support absolute current densities, $J \sim 0.02 \text{ A cm}^{-2}$ with deposits resembling the dendritic morphology of those produced

from hematite slurries.¹⁴ The formation of dendrites at Fe films has previously been attributed to both solid-state and dissolution-redeposition mechanisms.^{15,16}

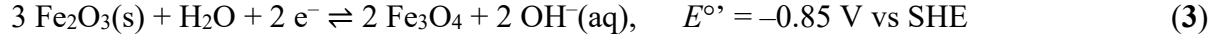
Dissolved species transport likely limit the role of soluble reactants dissolved in bulk electrolyte during Fe growth at absolute current densities $> 0.1 \text{ A cm}^{-2}$.^{17,18} For this reason, many have suggested a reaction pathway that bypasses dissolved Fe species,^{19,20} but the experimental evidence supporting a solid-state mechanism is incomplete. Magnetite (Fe_3O_4) and metallic Fe



Scheme 1: Chemical and electrochemical conversion reactions associated with the reduction of Fe_2O_3 to Fe at low temperatures. Solid-liquid equilibria are shown by blue arrows and electrochemical reduction steps are shown by yellow arrows.

have been observed via *ex-situ* Mössbauer spectroscopy within reactant $\alpha\text{-Fe}_2\text{O}_3$ particles following reduction at -1.2 V vs Hg/HgO in 50 wt.% NaOH at 100°C , which seems to support a solid-state reaction pathway (**Scheme 1** $\text{i} \rightarrow \text{iii} \rightarrow \text{v}$).²¹ Moreover, epitaxial Fe_3O_4 films grown on Au convert to epitaxial Fe metal, but without direct measurements of intermediate products the mechanism could not be resolved.¹⁹

The formal potential, E° , is the most convenient thermodynamic descriptor for Fe_2O_3 to Fe reactions (**Equation 2–4**) because the activity coefficient of OH^- and H_2O is dependent on the cell temperature (as well other dissolved species) and is an important variable in concentrated and heated electrolytes relevant to energy storage and electrowinning.²² The estimated E° for various conversion reactions, assuming $[\text{OH}^-] = 10 \text{ M}$, are provided in **Equations 2–4**. (**Supporting Information, Table S1, S2**)



Dissolution-redeposition mechanisms will include at least one dissolved ferric/ferrous hydroxide couple,^{14,23–25} with OH^- produced as the deoxygenation product (**Equation 5–6**). We assume $\text{Fe}(\text{OH})_4^{2-}(\text{aq})$ to be the dominant ferrous species in concentrated hydroxide at $T < 100$ °C.¹⁰ $E^{\circ'}$ for reactions involving dissolved iron species was calculated assuming $[\text{Fe}(\text{OH})_4]^{2-} = [\text{Fe}(\text{OH})_4]^- = 1 \text{ mM}$ although we note that the saturated concentration of both species is a function of the temperature, $[\text{NaOH}]$, and electrode potential.^{10,26}



Most experimental reports of the direct conversion of $\alpha\text{-Fe}_2\text{O}_3$ primarily focus on commercial Fe_2O_3 powders,^{8,24,27,28} but a few studies have used naturally occurring iron oxide ores that are predominately dense $\alpha\text{-Fe}_2\text{O}_3$ with Fe_3O_4 , silica, and alumina impurities, due to their practical relevance and abundance.²¹ Pressed pellets of Fe_2O_3 , Fe_3O_4 , and mixed Fe-Al ceramics have been explored as cathodes for alkaline iron reduction,^{29–31} where the micron-scale porosity within the bulk pellet has been shown to have a significant influence on the electrode kinetics. Studies of individual ore particles revealed geometric trends in the growth of Fe around the particle surface as well as apparent limits to conversion as a function of particle diameter.²¹ Very little data exists, however, on the intrinsic reduction kinetics of fully-dense (ore-like) $\alpha\text{-Fe}_2\text{O}_3$ particles in the absence of transport restrictions or impurities which influence the reaction selectivity.³²

Furthermore, while the role of particle size has been frequently discussed,^{20,21,25} the influence of nanoscale porosity has received less attention and is rarely quantified for reactant $\alpha\text{-Fe}_2\text{O}_3$.

Fe negative electrodes generally limit the power density of secondary iron-air batteries for long-duration energy storage.^{33,34} While electrodes for oxygen evolution and oxygen reduction can operate at high rates ($|J| > 0.10 \text{ A cm}^{-2}$), Fe electrodes are most often cycled at $|J| < 0.05 \text{ A cm}^{-2}$ to avoid passivation by insulating oxide phases and parasitic hydrogen evolution.^{34,35} The specific surface area and chemical composition of Fe electrodes evolve with repeated cycling,³⁶ and the lifecycle of these electrodes is believed to terminate with the formation of micron-scale $\gamma\text{-Fe}_2\text{O}_3$ crystals with low electrical conductivity. Dissolved Fe species have long been hypothesized to play an important role in charging/discharging mechanisms for secondary iron electrodes,^{3,34,37,38} but measurements of dissolved intermediates within the cell environment are rarely reported.

In this study, we prepare a set of high-purity $\alpha\text{-Fe}_2\text{O}_3$ precursors to investigate how the nanoscale morphology of oxides influences the mechanism and rate of metal-oxide-to-metal conversion reactions. Molten-salt annealing of synthetic $\alpha\text{-Fe}_2\text{O}_3$ particles to prepare dense, micron-scale $\alpha\text{-Fe}_2\text{O}_3$ phases enabled direct comparisons of porosity and reactivity at moderate temperatures. Rotating-ring-disk-electrode (RRDE) measurements were used to quantify dissolved Fe intermediates during electrodeposition reactions from $\alpha\text{-Fe}_2\text{O}_3$ in concentrated NaOH for the first time. Correlated electron microscopy measurements revealed distinct oxide-to-metal pathways that were influenced by the morphology of the reactant oxide, including a new form of electrochemical milling.

Results

Characterization of $\alpha\text{-Fe}_2\text{O}_3$ reactants

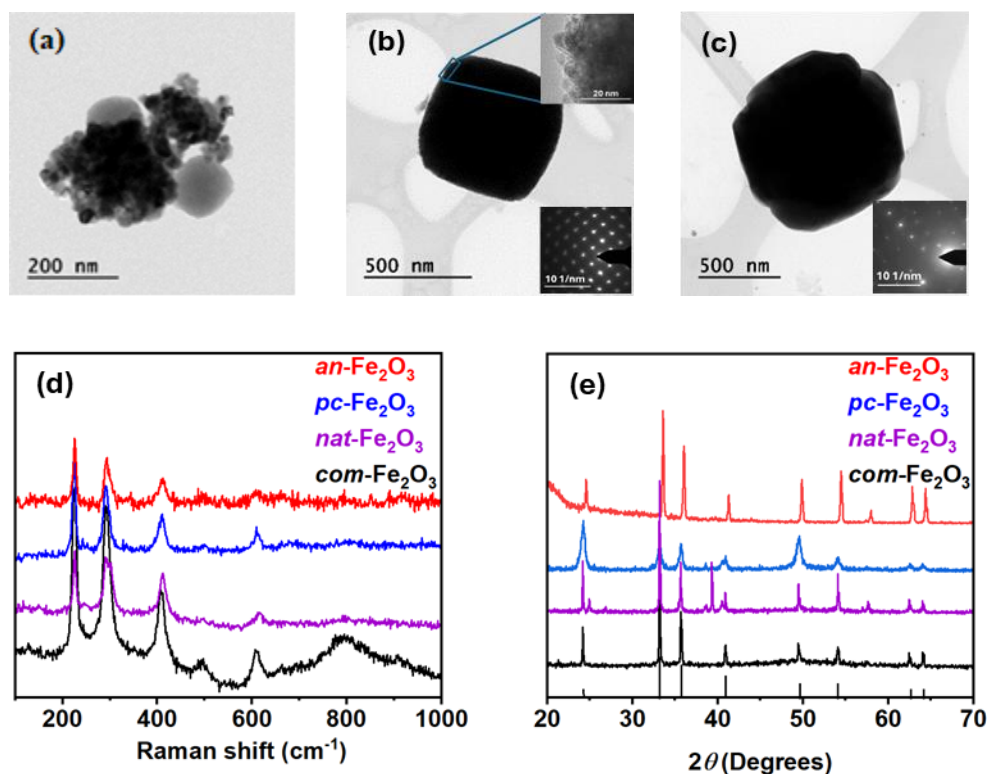


Figure 1: Dark field TEM images of (a) *com*-Fe₂O₃ particles (b) *pc*-Fe₂O₃ (upper and lower insets HRTEM image and SAED pattern, respectively) (c) *an*-Fe₂O₃. (d) Raman spectra and (e) Powder XRD of *com*-Fe₂O₃, *nat*-Fe₂O₃, *pc*-Fe₂O₃, and *an*-Fe₂O₃.

Hematite particles were first characterized via scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD), and Raman prior to electrochemical reduction (**Fig. 1**). Commercial α -Fe₂O₃ (*com*-Fe₂O₃) consisted of a polydisperse set of particles of varied morphology (**Fig. 1a**). The largest individual particles were ~200 nm diameter, but nanoparticles as small as 20 nm in diameter were present within agglomerates. These particles pose practical challenges for investigating reactions potentially controlled by surface area or solid-state diffusion. Therefore, we synthesized a set of homologous α -Fe₂O₃ particles having similar diameters but tunable morphology, following a previously reported method for synthesizing pseudo-cubic α -Fe₂O₃ (*pc*-Fe₂O₃, **Supporting Information**).³⁹ A subset of these particles was heated at 1000 °C under N₂ atmosphere to produce annealed particles with only a few crystalline domains (*an*-Fe₂O₃).

As-prepared *pc*-Fe₂O₃ particles ranged in diameter from 0.2 to 0.9 μm with an average diameter of 0.5(1) μm ($N = 208$, **Fig. 1b**, **Fig. S1-S2**). The larger *pc*-Fe₂O₃ particles visible in SEM were composed of smaller 15–25 nm α -Fe₂O₃ domains, as evident from transmission electron microscopy images (TEM, **Fig. 1b**). Analysis of the diffraction data using the Scherrer equation indicated that the average crystalline domain size within *pc*-Fe₂O₃ particles is 16 nm, which was consistent with the primary particle size observed via HRTEM (**Fig. 1b**, **Table S3**) and SEM (**Fig. S3**). The selected area electron diffraction (SAED) patterns from the edges of intact particles (**Fig. S1c**) as well as lamella prepared from an unreacted particle (**Fig. S4**) indicated that the primary particles were uniformly oriented with respect to the faces of the pseudocubic secondary particles. After annealing, the size distribution of *an*-Fe₂O₃ particles was consistent with the precursor *pc*-Fe₂O₃ (**Fig. S5**), but the particles were faceted, nanocrystalline domains were no longer observed at the particle edges (**Fig. 1c**, **Fig. S6-S7**, **Table S4**), and only a few, separately oriented, crystalline domains were detected in the SAED pattern from a lamella (**Figure S8**).

Raman spectroscopy (**Fig. 1d**) and powder X-ray diffraction (**Fig. 1e**) were used to compare the composition of the as-prepared Fe₂O₃ reactants. The *nat*-Fe₂O₃ particles yielded two small diffraction peaks at $2\theta = 25^\circ$ and 57° . A peak at $2\theta = 57^\circ$ was also observed for *an*-Fe₂O₃ and was assigned to the (018) reflection of the hematite structure, with the absence of this feature in the diffraction patterns for *pc*-Fe₂O₃ and *com*-Fe₂O₃ attributed to reduced crystallinity within the particles. The diffraction peaks resulting from long-range order are broader and difficult to resolve as the crystallite size is reduced.⁴⁰ The thermally annealed *an*-Fe₂O₃ and *nat*-Fe₂O₃ have large crystallites and show long-range order diffraction in comparison to *pc*-Fe₂O₃ and *com*-Fe₂O₃. All iron-oxide samples yielded a similar set of peaks in their Raman spectra, except for two broad peaks observed for *com*-Fe₂O₃ at $\sim 500\text{ cm}^{-1}$ and $\sim 800\text{ cm}^{-1}$, assigned to the A_{1g} mode and an

amorphous impurity phase, respectively.⁴¹ The relative intensities of the peaks at 225 cm⁻¹ and 293 cm⁻¹ were increased for *nat*-Fe₂O₃ relative to *pc*-Fe₂O₃ and *com*-Fe₂O₃ but comparable for *an*-Fe₂O₃, which we attribute to the larger crystallite size of *nat*-Fe₂O₃ compared to other α -Fe₂O₃ particles.⁴¹

Ex-situ SEM and TEM analysis of α -Fe₂O₃ particles

Figure 2 presents the chemical and morphological changes to α -Fe₂O₃ particles supported on polished, polycrystalline Au after electrochemical reduction in 10 M NaOH. The initial number density of Fe₂O₃ particles measured via SEM was ~ 15 per 100 μm^2 (**Fig. 2a,e**) but after reduction at $E = -1.3$ V for 5 min, the original *pc*-Fe₂O₃ particles were surrounded by 800 particles per 100 μm^2 of nanoparticles < 100 nm in diameter (**Fig. 2b, Fig. S9**). The fractional iron content (at%) measured via SEM energy dispersive x-ray spectroscopy (SEM-EDS) confirmed that the particles were deoxygenated from an initial composition consistent with Fe₂O₃ (40 at% Fe) to a final composition of 64 at% Fe (**Fig. S9, Table S5**). In contrast, similar treatment of *an*-Fe₂O₃ particles did not lead to the formation of visible nanoparticles via SEM or EDS on the Au substrate, (**Fig. 2e,f**), but a subset of particles fractured to form a small collection of nanoparticles with a high Fe at% in the same spatial area as the original *an*-Fe₂O₃ particle (**Fig. S10**).

The structure and composition of the reacted nanoparticles were characterized using dark-field TEM (**Fig. 2c,g**) and EDS mapping (**Fig. 2d,h**). Nanoparticles, 40–100 nm in diameter and having an Fe content of 80 at% Fe (**Fig. S11**), were visible in the regions adjacent to the parent *pc*-Fe₂O₃ particles supported on the TEM grid were all found to deoxygenate, only fractured particles exhibited elemental composition with >90 at% Fe (**Fig. 2h**). A few of the reacted *pc*-Fe₂O₃ particles were excised from TEM grids and cross-sectioned using a gallium focused ion beam for further analysis of the morphological and compositional changes occurring during reduction.

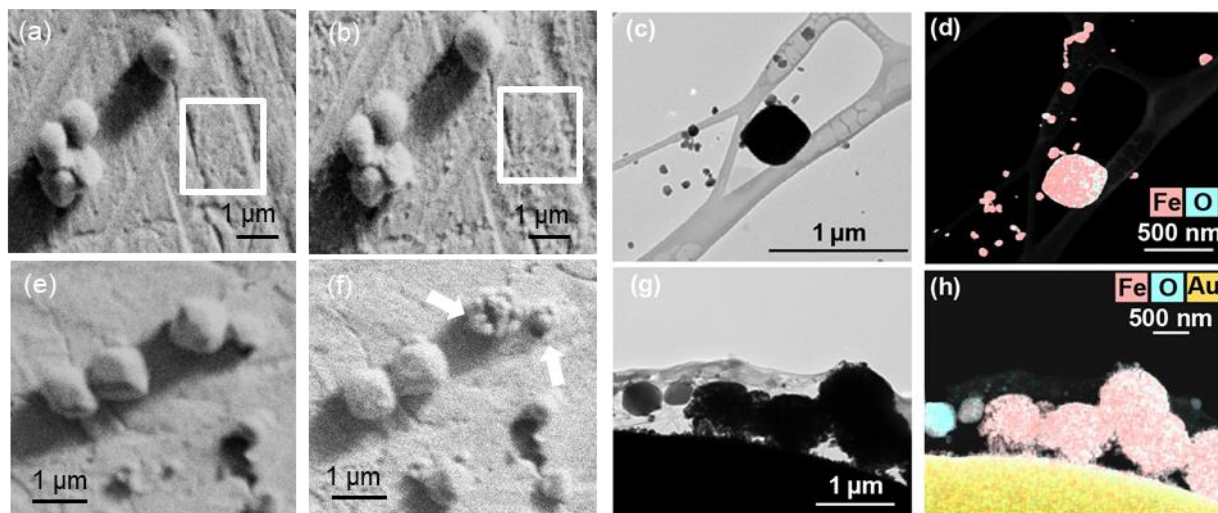


Figure 2: Representative correlated SEM images of (a,b) *pc*-Fe₂O₃ and (e,f) *an*-Fe₂O₃. A polycrystalline Au electrode was imaged (a,e) as-deposited and (b,f) after reduction. TEM-EDS images of (c,d) *pc*-Fe₂O₃ and (g,h) *an*-Fe₂O₃ after reduction. Reduction of the films occurred at -1.3 V vs Hg/HgO in 30 wt.% NaOH in H₂O at 80 °C under N₂. A Au TEM grid served as a working electrode.

Figure 3 presents a cross-sectional TEM image of a single *pc*-Fe₂O₃ particle after reduction at -1.3 V vs Hg/HgO at 80 °C. As compared to an unreacted *pc*-Fe₂O₃ particle, the reduced oxide particles contained interconnected channels which extended from the surface to the particle core (**Fig. 3a–b**). The maximum pore width, measured across lighter contrast regions, exceeded 15 nm, in contrast the unreacted particle which showed no visible pores (**Fig. S4**). SAED patterns collected from these particles revealed a nanocrystalline oxide that could be assigned to either Fe₃O₄ or γ -Fe₂O₃ but Fe metal was not detected within the boundaries of the reduced particle (**Fig. 3c**).

Figure 4a displays a cross-section of a single, reduced and fractured *an*-Fe₂O₃ particle after reduction at $E = -1.3$ V vs Hg/HgO. In contrast to the dense, unreacted *an*-Fe₂O₃ (**Fig. S6**, **Fig. S8**), reduced and fractured particles contained large cracks extending the full particle radius. EDS mapping revealed that the fractured particle was almost completely deoxygenated except for a thin layer of oxide present along fissures, which we attribute to a passivation layer formed during

transfer from the cell and between microscopes (**Fig. S12**). Similar behavior was observed across multiple Fe_2O_3 particles reduced on TEM grids, but not all deoxygenated particles were observed to fracture (**Fig. S13**). Analysis of inverse pole figure maps (IPF, **Fig. S14c**) acquired using TKD mapping (**Fig. S14b**) indicated that the particles were bcc-Fe with random lattice orientations with

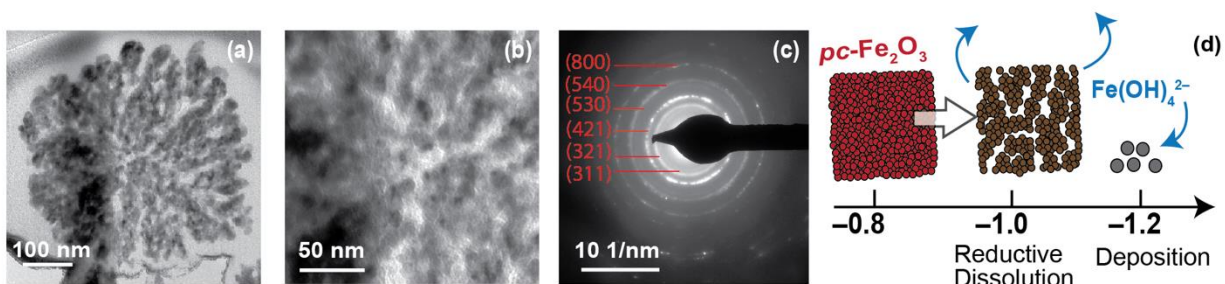


Figure 3: (a) TEM images of a cross-section of $pc\text{-Fe}_2\text{O}_3$ after reduction at -1.3 V vs Hg/HgO. in 30 wt.% NaOH at 80 °C. (b) Zoom-in image of (a). (c) SAED pattern of the cross-section. (d) Scheme representing the mechanism of reduction of $pc\text{-Fe}_2\text{O}_3$.

respect to the electrode surface normal. The d-spacing calculated from zone axis high-angle annular dark field (HAADF) micrographs also confirmed the presence of bcc-Fe (**Fig. 4e**).

A partially reduced particle, in contact with the larger Fe particles, was inspected for features which might support a reactive mechanism in dense Fe_2O_3 (**Fig. 4b**). TKD and HAADF-STEM imaging of a partially reacted particle (**Fig. S15**) adjacent to the fractured Fe particle revealed a cubic inverse spinel structure, which is most consistent with Fe_3O_4 , although the presence of $\gamma\text{-Fe}_2\text{O}_3$ could not be ruled out. Brighter regions were surrounded by small spots, only a few nm in diameter (**Fig. 4c**), that were revealed to be Fe-rich via EDS mapping (**Fig. 4d**). Larger Fe domains within the $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ particle were consistent with bcc-Fe, based on TKD measurements (**Fig. S15c**) and the d-spacing of lattice fringes (**Fig. 4f**).

Thin film voltammetry of $\alpha\text{-Fe}_2\text{O}_3$

We next employed thin-film voltammetry to probe the electrochemical steps involved in the multielectron reduction of α - Fe_2O_3 . The mass-loading of Fe_2O_3 ($43 \mu\text{g cm}^{-2}$) was held constant across experiments and was selected to produce sub-monolayer films of particles on glassy carbon, which minimized the influence of water reduction and localized the current response to particles in direct electrical contact with the electrode (**Fig. S16**). Reduction of α - Fe_2O_3 yielded morphology-dependent current-voltage (i - E) responses in 10 M NaOH during the first cyclic voltammogram at 5 mV s^{-1} (**Fig. 5**).

The onset of cathodic current ($E < -0.9 \text{ V}$) occurred earlier for pc - Fe_2O_3 compared to an - Fe_2O_3 ($E < -1.17 \text{ V}$). The pc - Fe_2O_3 voltammetry also featured two distinct cathodic waves with a peak gravimetric current of -3.0 mA cm^{-2} at $E_p = -1.19 \text{ V}$, whereas only a single cathodic wave, lacking a well-resolved peak, was measured at an - Fe_2O_3 films (**Fig. 5b**). Two additional an - Fe_2O_3 particles, partially annealed for 1 and 2 h, respectively, were prepared to understand the impact of defects and crystalline domain size on the initial activity of α - Fe_2O_3 (**Fig. S17**). All annealed particles showed similar gravimetric

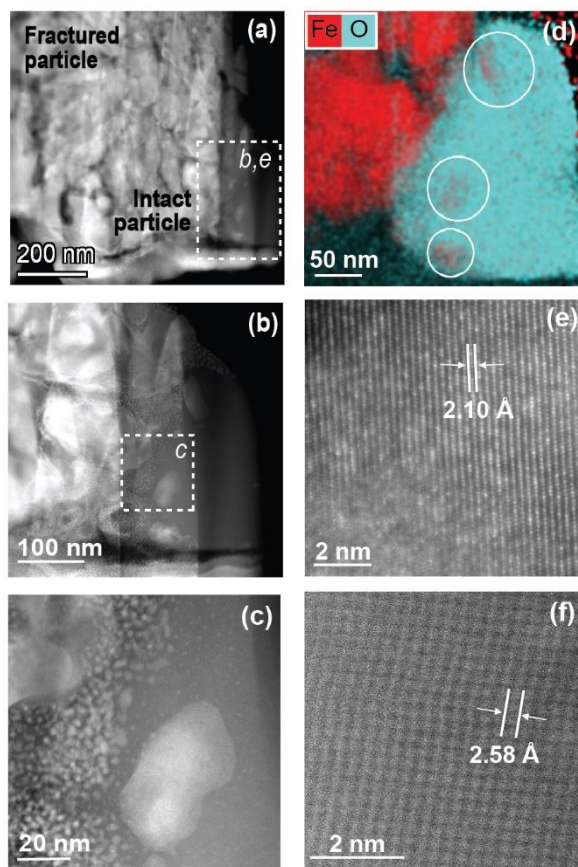


Figure 4: (a) HAADF-STEM image showing the cross-section of a fractured an - Fe_2O_3 and intact particle after reduction at -1.3 V in 30 wt.% NaOH at 80°C . (b) HAADF-STEM image of the intact particle and the junction. (c) Zoom-in image of the section shown in (b). (d) EDS map of Fe and O content in the corner section of the intact particle shown in (b). (e) atomic-resolution HAADF-STEM micrograph of the fractured particle obtained along $\langle 110 \rangle$ zone axis. (f) atomic-resolution HAADF-STEM micrograph of the intact particle obtained along $\langle 311 \rangle$ zone axis.

surface areas, indicating that the treated Fe₂O₃ particles possessed a dense, crystalline surface that was free of accessible pores (Table S6). Prior to complete annealing, Fe₂O₃ particles yielded larger cathodic current at $E_p \sim -1.19$ V which was directly proportional to the annealing time. The geometric current density for all particles exceeded the expected mass-transport-limited current density (i_l) for a dissolved three-electron reactant at 5 mM ($i_l = -0.3 \text{ mA cm}^{-2}$, Supporting Information). The integrated cathodic charge for Fe reduction, Q_{Fe} , was calculated from the current prior to the onset of water reduction (Equation 7),

$$Q_{\text{Fe}} = 1/\nu \int_{-0.9}^{-1.23} i \, dE \quad (7)$$

where ν represents the scan rate. Q_{Fe} was 3 mC

and 1 mC for the *pc*-Fe₂O₃ and *an*-Fe₂O₃ particles, respectively, which was sufficient to reduce 28% and 9% of the initial Fe₂O₃ loading to Fe(0). Qualitatively similar trends in voltammetry were observed across *com*-Fe₂O₃ and *pc*-Fe₂O₃, with both samples yielding two separate reduction waves with a peak gravimetric current of -1.5 mA cm^{-2} at $E_p = -1.16$ V (Fig. 5a). Q_{Fe} for *com*-Fe₂O₃ was 30%. A thin film prepared from natural Fe₂O₃ (*nat*-Fe₂O₃, Fig. S18) showed the lowest activity of all particles, despite the presence of nanometer-scale fines, with an onset of cathodic

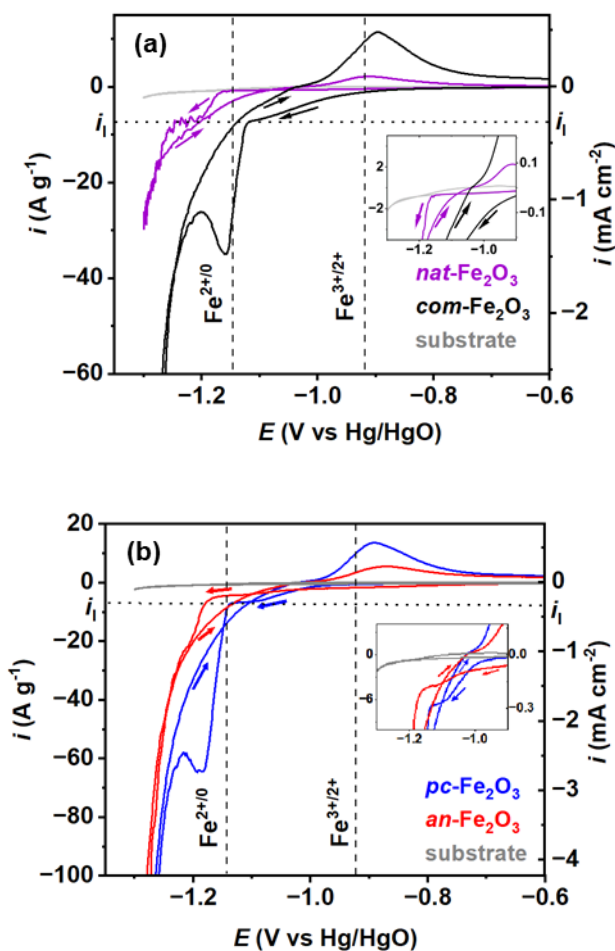


Figure 5: Voltammetry of glassy carbon electrode and glass carbon electrodes modified with thin films ($43 \mu\text{g cm}^{-2}$) of (a) *nat*-Fe₂O₃ and *com*-Fe₂O₃ and (b) *pc*-Fe₂O₃ and *an*-Fe₂O₃ in 30 wt.% NaOH at 80 °C at $\nu = 5 \text{ mV s}^{-1}$. E° for Equations 5–6 under the reaction conditions are indicated as dotted black lines. i_l is mass transport limiting current.

current at $E < -1.17$ V. Although water reduction at $E < -1.2$ V prevented measurements of Fe reduction kinetics, the oxidation of a reduced Fe species was evident in the positive return sweep for all particles and substantially more reversible charge towards Fe was passed for *com*-Fe₂O₃ and *pc*-Fe₂O₃ compared to *nat*-Fe₂O₃ and *an*-Fe₂O₃ (**Supporting Information**). Surprisingly, *an*-Fe₂O₃ particles showed an opposite response to the presence of convection within the cell as compared to *pc*-Fe₂O₃ and *com*-Fe₂O₃ particles (**Fig. S19**), attributed to different roles of dissolved intermediates across the two particles.

Thin film RRDE of α -Fe₂O₃ samples

We used a rotating ring disk electrode (RRDE) to directly quantify the role of dissolved Fe³⁺ and Fe²⁺ intermediates during Fe₂O₃ reduction. We calculated the mass transport limited current density (i) during forced convection at the rotating disk to be -2.3 mA cm^{-2} . A glassy-carbon ring electrode allowed for the selective oxidation of Fe²⁺ over competing H₂ oxidation and thus was used to continuously monitor the rate of formation of soluble Fe²⁺ (**Supporting Information**). **Fig. 6a** presents the voltametric response of thin film *com*-Fe₂O₃, *pc*-Fe₂O₃, and *an*-Fe₂O₃ during rotation at 1000 rpm in 30 wt.% NaOH at 80 °C. During continuous forced convection, *pc*-Fe₂O₃ and *com*-Fe₂O₃ films no longer produced substantial cathodic currents at $E > -1.0$ V and also did not show a clearly resolved current maximum. However, the onset of Fe³⁺ reduction was apparent at the ring, which showed an onset of Fe²⁺ formation at $E < -0.93$ V and -1.0 V, for *com*-Fe₂O₃ and *pc*-Fe₂O₃ particles, respectively, when the ring was held at an oxidative potential (-0.3 V vs Hg/HgO) (**Fig. 6b**). In contrast, *an*-Fe₂O₃ films yielded a previously unresolved cathodic peak at $E_p = -1.15$ V but a similar, gradual onset in i_R at $E > -1.1$ V was not observed. Instead, as a sharp peak i_R occurred at $E = -1.15$ V. For all particles, i_R approached 0.0 mA cm^{-2} for $E < -1.2$ V.

The current efficiency towards soluble Fe^{2+} species ($\eta_{\text{Fe}^{2+}}$) which could be detected at the ring was calculated as $\eta_{\text{Fe}^{2+}} = \frac{i_R}{i_D N_c}$, where N_c is the collection efficiency ($36 \pm 4 \%$) calibrated in 30 wt.% NaOH using $\text{Ru}^{2+/3+}$ (as RuCl_3) as a soluble redox couple in alkali (**Fig. S20**). The fraction of soluble Fe^{2+} collected was highest for *com*- Fe_2O_3 and was near zero for *an*- Fe_2O_3 particles. The maximum value of $\eta_{\text{Fe}^{2+}}$ for *com*- Fe_2O_3 particles occurred at $E = -1.08 \text{ V}$ where $\eta_{\text{Fe}^{2+}}$ 89% (**Fig. 6c**), such that most of the disk current could be assigned to reductive dissolution. The maximum value of $\eta_{\text{Fe}^{2+}}$ for the *pc*- Fe_2O_3 was 33% at $E = -1.15 \text{ V}$ and 3% for *an*- Fe_2O_3 at $E = -1.13 \text{ V}$. In this potential region, both i_R and i_D increased slightly with increasing rotation rates (**Fig. S21**). This finding is inconsistent with mechanisms involving a dissolved intermediate that promotes reductive dissolution. Similar ring-disk-electrode measurements with 50 wt% NaOH serving as the supporting electrolyte led to a >15-fold increase in i_D and a limiting current was observed for $E > -1.15 \text{ V}$

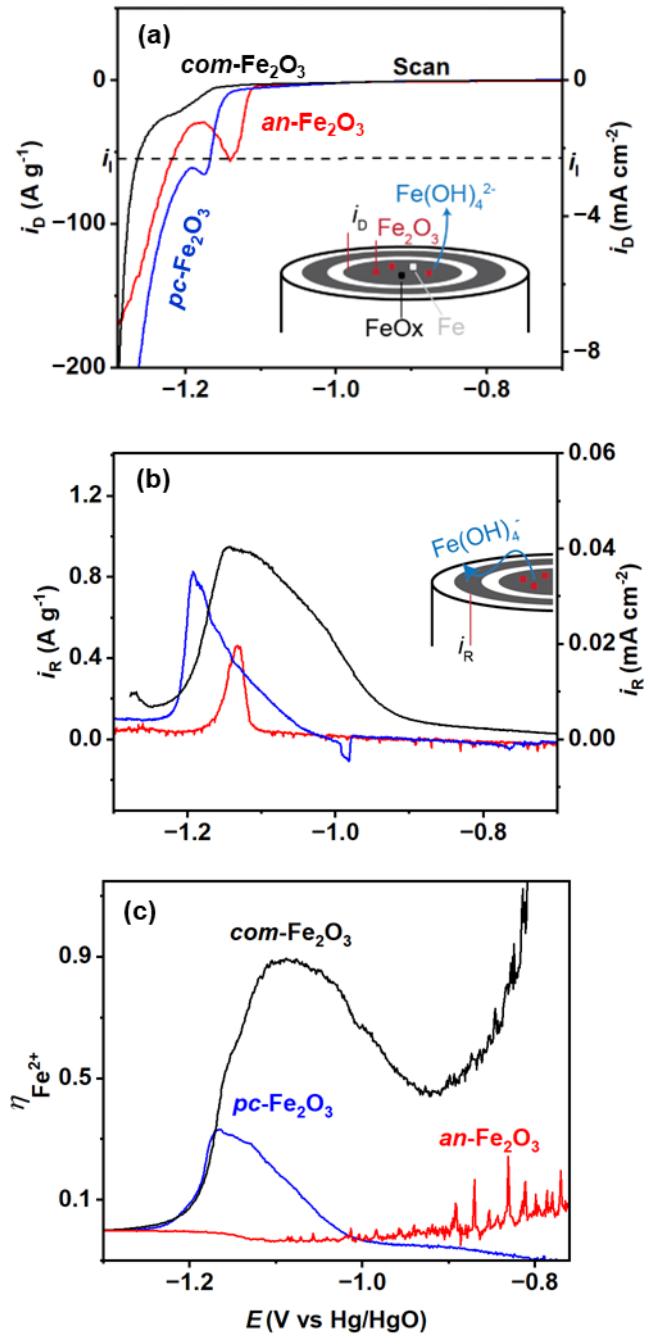


Figure 6: RRDE of thin film Fe_2O_3 (43 $\mu\text{g cm}^{-2}$) in 30 wt.% NaOH at 80 $^{\circ}\text{C}$. (a) Disk current (a) and ring current ($E -0.3 \text{ V}$) (b) during negative potential sweep. (c) The fraction of soluble Fe^{2+} ($\eta_{\text{Fe}^{2+}}$) formation. Scan rate = 5 mV s^{-1} and rotation rate = 1000 rpm. i_l is mass transport limiting current.

(Fig. S22) with further increases to i_D at $E < -1.15$ V leading to the disappearance of Fe^{2+} at the ring.

Measurements of Fe^{2+} during the positive sweep (Fig. S23a), revealed that oxidation of Fe to Fe^{2+} occurred at $E > -0.9$ V and Fe^{2+} was no longer detected for $E > -0.80$ consistent with the formation of Fe^{3+} and/or insoluble Fe^{2+} oxides or hydroxides. When the ring electrode was biased to reduce Fe^{3+} , a cathodic wave was observed (Fig. S23b) indicating the presence of soluble Fe^{3+} . The oxidation current measured on the positive return sweep was highest for Fe films produced from *pc*- Fe_2O_3 followed by *an*- Fe_2O_3 and *com*- Fe_2O_3 particles and the amount of Fe^{2+} collected at the ring from *pc*- Fe_2O_3 was $\sim 2\text{X}$ greater than the collection from *an*- Fe_2O_3 and *com*- Fe_2O_3 particles. Ferric species were measured at a ring biased to $E = -1.1$ V, which revealed that while Fe^{3+} was generated during the oxidation of Fe, the current remained relatively constant throughout the reduction of *pc*- Fe_2O_3 (Fig. S24).

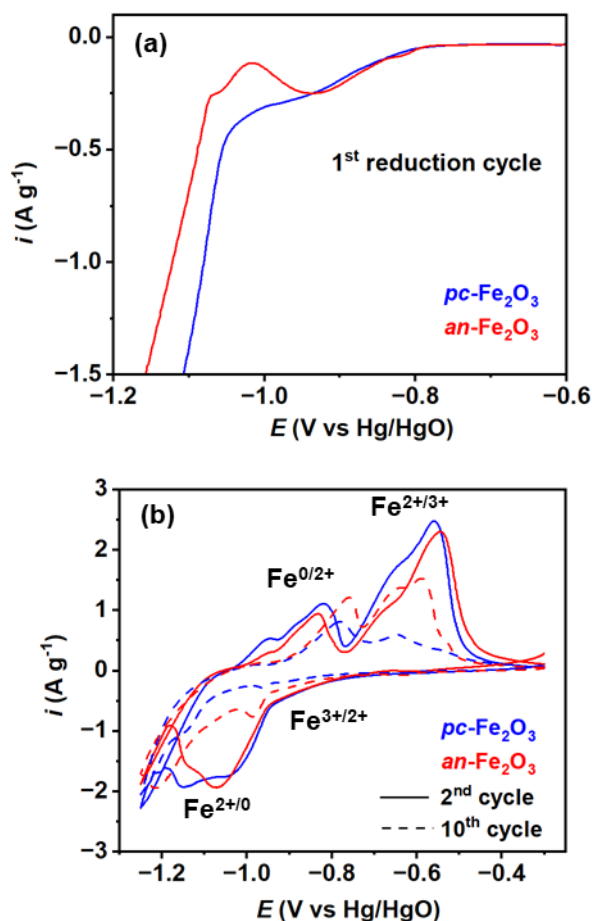


Figure 7: CV cycling behavior of battery type electrodes with *pc*- Fe_2O_3 and *an*- Fe_2O_3 at mass loadings $6\text{--}8\text{ mg cm}^{-2}$. (a) The first negative potential scan is compared to the (b) the second (solid line) and tenth (dashed line) CV cycles.

Electrochemical response of Fe_2O_3 in battery-type electrodes

Figure 7 presents the voltametric behavior of *pc*-Fe₂O₃ and *an*-Fe₂O₃, deposited from a slurry at a loading of 6–8 mg cm⁻² and then cycled in a representative alkaline battery electrolyte (room temperature 8 M KOH and 1 M LiOH).³⁶ The *i*-*E* response of α-Fe₂O₃ at $\nu = 0.5 \text{ mV s}^{-1}$ and high mass-loadings revealed morphology-dependent cycling and capacity retention that are relevant to long-duration-energy-storage applications of Fe. Similar onset potentials for cathodic current ($E \sim -0.8 \text{ V}$) were observed and the current response for *an*-Fe₂O₃ featured a distinct cathodic wave centered at -0.95 V whereas *pc*-Fe₂O₃ lacked a well-resolved peak in this potential region. At $E < -0.95 \text{ V}$, *pc*-Fe₂O₃ produced cathodic currents that were twice those measured for *an*-Fe₂O₃ electrodes. Electrodes prepared from *pc*-Fe₂O₃ particles after 1 and 2 hours of annealing did not yield substantial differences in comparison to *an*-Fe₂O₃ (3 hours annealing).

The anodic specific capacity (C_a) was integrated from $-1.0 \text{ V} < E < -0.3 \text{ V}$ during the positive potential scan and normalized to the mass of Fe (**Fig. S25**). Two major oxidation peaks were observed at $E = -0.78 \text{ V}$ and -0.60 V , which have previously been assigned to Fe^{0/2+} and Fe^{2+/3+} redox reactions,^{24,36} were more prominent for *pc*-Fe₂O₃ compared to *an*-Fe₂O₃ particles, and for all particles the total integrated charge for Fe oxidation ($E < -0.7 \text{ V}$) was typically less than half the charge passed for Fe^{2+/3+}. Although micron-scale oxide particles generally did not lead to high specific capacities, *an*-Fe₂O₃ electrodes consistently exhibited increased cycling stability relative to *pc*-Fe₂O₃ electrodes in room temperature KOH/LiOH electrolytes. The total anodic specific capacity of *pc*-Fe₂O₃ decreased from 337 to 131 mAh g⁻¹ over 10 cycles but *an*-Fe₂O₃ decreased from 301 to 131 mAh g⁻¹ (**Fig. S25**). Repeated conversion reactions during electrochemical cycling led to substantial changes to the composition and morphology of *pc*-Fe₂O₃ and *an*-Fe₂O₃ particles. XRD analysis of post-cycle electrodes revealed the presence of Fe₃O₄ or γ-Fe₂O₃ along with Fe metal (**Fig. S26**). Clusters of Fe-rich (>70 at%, EDX) domains, 5-10 μm in

length were produced from *pc*-Fe₂O₃ films (**Fig. S27a,b**), whereas *an*-Fe₂O₃ particles appeared to form smaller domains of Fe-rich regions relative to the parent particles (**Fig. S27c,d**).

Discussion

Morphology and electrochemical activity of synthetic Fe₂O₃ particles

Porous α -Fe₂O₃ and dense α -Fe₂O₃ particles having similar particle diameters allowed the influence of nanoscale morphology on electrochemical activity to be directly quantified. Both *pc*-Fe₂O₃ and *com*-Fe₂O₃ shared qualitative similarities in morphology that are related to their recent precipitation from dissolved species, whereas *an*-Fe₂O₃ particles were denser and exhibited similar structural signatures with *nat*-Fe₂O₃ (**Fig. 1c, 1e, S6, S7**). Thin films of *pc*-Fe₂O₃ and *com*-Fe₂O₃ were reduced at the most positive *E* in the absence of forced convection, whereas *an*-Fe₂O₃ and *nat*-Fe₂O₃ particles were electrochemically inert for *E* > -1.0 V (**Fig. 5a–b**). All particles produced cathodic currents at *E* < -1.1 V, but a cathodic current peak was only observed for *pc*-Fe₂O₃ and *com*-Fe₂O₃. We assign this peak to reductive dissolution of α -Fe₂O₃ based on the onset potential, which can lead to Fe plating from Fe(OH)₄²⁻. Gravimetric activity towards reductive dissolution appears to be strongly sensitive to the presence of nanoscale pores.

Correlated SEM and TEM images before and after electrochemical reduction at potentials sufficient to reduce α -Fe₂O₃ to Fe metal support a dissolution-redeposition mechanism for *pc*-Fe₂O₃ (**Fig. 2, 3**). The Fe-rich particles, 40–100 nm in diameter, observed in the vicinity of parent particles (**Fig. 2b,c**) were larger than the primary particles observed via SEM (15–25 nm, **Fig. S3, Fig. S9**), and thus could not have been formed via direct conversion of primary α -Fe₂O₃ given the difference in molar volume (Fe basis) of α -Fe and α -Fe₂O₃ (**Supporting Information**). The absence of any particles having *d* < 25 nm is thus evidence of Fe metal formation via dissolved

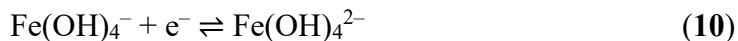
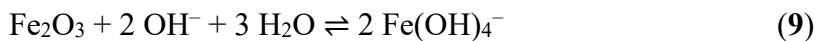
ferrous species. Dissolution was also associated with increased pore widths following reduction which could facilitate the transport of dissolved intermediates (**Fig. S11, Fig. 3a,b**). Although ex-situ diffraction patterns were consistent with either Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$, these phases could have been formed external to the electrochemical cell. Likewise, Fe nanoparticles less than 10 nm in diameter could potentially oxidize after being removed from the electrochemical cell and future studies should probe the surface of $\text{Fe}_2\text{O}_3/\text{Fe}$ in the reaction environment. The increased activity towards reductive dissolution in *pc*- Fe_2O_3 could either be caused by a lower kinetic barrier for conversion due to smaller Fe_2O_3 domains or a more effective coupling of electronic- and ionic conductivity through the nanoporous films. The thermodynamics of ion transfer in solid phases is expected to depend on the particle size for domains smaller than < 100 nm and neutron diffraction studies at Li_xTiO_2 have shown that lithiation primarily proceeds through complete conversion of nanoscale domains.⁴² On the other hand, the electrical properties of $\alpha\text{-Fe}_2\text{O}_3$ thin films are influenced both by the particle size and annealing temperature,⁴³ and the apparent conductivity of thin films of nanoparticles increases with decreasing particle diameter.⁴⁴

Dense oxide particles exhibit features more consistent with direct conversion of oxides to metal. Intermediate oxides (Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$) and $\alpha\text{-Fe}$ were observed within the original phase boundaries of *an*- Fe_2O_3 particles as indicated by the TKD (**Fig. S14b, S15c**) and EDS mapping (**Fig. 4d and Fig. S12, S15d,e**). Formation of $\alpha\text{-Fe}$ was always accompanied by particle fracture, with intact particles showing increased O content ($\text{Fe}:\text{O} = 4:1$, **Fig. S13**). Small Fe metal domains were observed in the same region as a larger partially reduced Fe_3O_4 phase, which is consistent with a chemomechanical mechanism where metal formation precedes fracture (**Fig. 4b,c**).⁴⁵ Simple estimations of the stresses associated with conversion and crack propagation suggest that the formation of Fe metal domains is necessary for fracture, and future work will investigate these

mechanisms in more detail (**Supporting Information**). Fracture was also positively correlated with larger particle diameters, which is suggestive of a stress-related mechanism driven by density differences in reduced oxides and metallic phases.^{46,47} This model is consistent with the electrochemical activities of particle at various extents of annealing, where the cathodic peak height at $E \sim -1.19$ V was inversely correlated with annealing time and potentially the initial size of cracks within the particles (**Fig. S17**). Size-dependent fracture has been reported in oxide shells formed at iron nanoparticles, which allows solvent and oxygen to drive continued reactions at the nanoparticle core.⁴⁸ We propose that intentional fracture driven by electrochemical cells represents a form of “electrochemical milling” which can drive size reduction in particles which are too small to be processed by conventional grinding and milling equipment.

Dissolved species during Fe₂O₃ reduction

The earlier onset of cathodic ring current ($E > -1.1$ V) for *pc*-Fe₂O₃ and *com*-Fe₂O₃ particles indicates that these oxides more readily form dissolved ferrous species. Because the i_D in this potential window is mostly constant, but diminished with transport of dissolved species away from the electrode surface, we assign this potential region to a dissolution-and-reduction mechanism (**Scheme 1 i→ii→iv→v**, **Equation 9–10**).



The dissolution-and-reduction mechanism is consistent with the observation of a greater limiting current when Fe₂O₃ is suspended in 50 wt.% NaOH (**Fig. S22**) due to the increasing solubility of ferrous with increasing [OH[−]] and inconsistent with a reductive-dissolution (**Scheme 1**

i→**iii**→**iv**→**v**) mechanism where removal of the dissolved intermediate would be expected to accelerate the chemical dissolution.

Greater than 65% of the charge passed at *pc*-Fe₂O₃ led to ferrous species which were not detected at the ring electrode (**Fig. 6c**). This irreversible charge, occurring at *E* positive of that necessary for Fe metal formation, could be reconciled by solid Fe^{2+/3+} oxides, either formed directly (**Scheme 1 i**→**iii**) or via dissolution and redeposition (**Scheme 1 i**→**ii**→**iv**→**iii**) onto the Au electrode surface. For *E* < -1.16 V, Fe metal is expected to be the predominate species at the electrode surface and cathodic charge passed will lead to direct metal formation or indirectly capture dissolved ferrous species at adjacent Fe nuclei. This behavior is evident in the loss of *i_R* and $\eta_{\text{Fe}^{2+}}$ commensurate with the increase in $|i_D|$ (**Fig. 6b, c**).

Cathodic currents that were present for *pc*-Fe₂O₃ and *com*-Fe₂O₃ particles at *E* > -1.1 V in stagnant cells were diminished to *i* < 0.05 A g⁻¹ during electrode rotation at 1000 rpm. Consistent with previous reports,⁸ we assign these currents to the electrochemical reduction of dissolved Fe³⁺ species, which would accumulate in the stagnant boundary-layer for a thin film, but are rapidly removed from the surface by forced electrolyte convection driven by rotation (**Fig. S19**). Nevertheless, for *pc*-Fe₂O₃ particles, the rate of Fe²⁺ formation prior to solid state reduction is >10-fold less than the peak current for Fe metal formation in the absence of forced convection (**Fig. 6a, c**).

Morphology dependent CV cycling behavior of synthetic Fe₂O₃ particles

The earlier onset of Fe^{3+/2+} reduction for *pc*-Fe₂O₃ and *an*-Fe₂O₃ in battery-type electrodes (**Fig. 7a**) compared to the thin-film measurements (**Fig. 5b**) is attributed to improved electrical contact across the surface of the particles and the current collector. Consistent with thin-film

measurements, *pc*-Fe₂O₃ shows higher gravimetric current at $E > -0.95$ V than *an*-Fe₂O₃. For both *pc*-Fe₂O₃ and *an*-Fe₂O₃, two distinct Fe^{0/2+} oxidation peaks were observed at $E = -1.0$ V and -0.78 V (**Fig. 7b**). We attribute the differences in potential to two distinct oxidation processes at iron metal (i.e. surface passivation at more negative E vs. bulk dissolution and redeposition at more positive E). Further evidence is present in ring-disk data of *pc*-Fe₂O₃ (**Fig. S23**), where a shoulder peak in the ring current is observed during the oxidation at -0.9 V $< E < -1.0$ V, prior to the peak in i_D . Small Fe nanoparticles, observed in the vicinity of converted *pc*-Fe₂O₃ (**Fig. 2b,d**) are a plausible source of this minor current response.

Analysis of the potential-dependent capacity for α -Fe₂O₃ particles indicates that at room temperature the formation of Fe⁰ is inhibited relative to the more facile cycling between Fe^{2+/3+} centers (**Fig. S26**). Although the three-electron specific capacity of α -Fe₂O₃ is 1007 mAh g_{Fe}⁻¹, <33% of this capacity was consistently measured during oxidation, suggestive of a predominately one-electron reduction process. Consistent with thin film electrochemistry (**Fig. 5b**), *pc*-Fe₂O₃ consistently yielded a greater initial C_a than *an*-Fe₂O₃, but repeated cycling led to a sharp decline in C_a . The steeper decline in C_a for *pc*-Fe₂O₃ may be attributed to the larger extent of passivation of highly porous iron metal during oxidation (**Fig. 3, Fig. S25**). The increased cycling stability of *an*-Fe₂O₃ (**Fig. S25**) indicates that oxides which minimize the formation of dissolved intermediates may prolong the cycling stability of metal/metal oxide anodes—assuming that reactive fracture can be avoided.

Comparisons to previous models for oxide-to-metal processes

We observe four major differences in the apparent mechanism for α -Fe₂O₃ reduction in alkaline media relative to previously reported mechanisms. First, we use RRDE measurements to find that for all Fe₂O₃ particles, soluble ferrous species are present within the reactive boundary

layer during the onset of Fe formation (**Fig. 6b**). This does not exclude the presence of a solid-state conversion mechanism but is direct evidence that soluble intermediates are consistently present during the initial stages of α -Fe₂O₃ reduction, even for dense Fe₂O₃ reactants. Apparent solid-state reduction mechanisms may still be mediated by trace dissolved intermediates which travel nanometer length scales between dissolving oxides and growing metal phases.¹² Second, for dense, ore-like particles, the Fe₂O₃-to-Fe pathway occurs primarily via an *apparent* solid-state reduction of particles (**Fig. 2h, 4a**), with fracturing particles strongly correlated with the formation of Fe. The presence of small Fe domains within intact oxide phases is suggestive of fracture induced by Fe growth; further studies are necessary to understand the mechanics of this process. Third, mechanisms of α -Fe₂O₃ reduction involving an initial non-faradaic dissolution step forming Fe(OH)₄⁻ appear to be inconsistent with the observed rates of Fe formation during electrowinning, as the transport-limited rate measured for ferric to ferrous reduction (**Fig. 6a,b**) is substantially smaller than the rate of reductive dissolution and/or iron metal formation (**Fig. 5**). Lastly, RRDE measurements suggest that dissolved ferrous species do not promote reductive dissolution of solid α -Fe₂O₃ (**Fig. S21**), but oxide dissolution may be accelerated during the formation of Fe due to the consumption of dissolved ferrous intermediates (**Fig. 6**), and the fracture of more crystalline oxide particles (**Fig. 4a**).

Implications for electrowinning and energy storage

Nanosized domains of α -Fe₂O₃ (**Fig. 3**) show substantially greater activity for reductive dissolution followed by plating (**Scheme 1 i→iii→iv→v**), compared to dense Fe₂O₃ particles (**Fig. 4**) which primarily form Fe via an *apparent* solid-state pathway coupled to reactive fracture. XRD and Raman spectra provide useful spectroscopic signatures and information about crystallite size and crystal structure that are correlated with reactivity trends (**Fig. 1d,e**). These findings are

consistent with studies showing increased activity during repeated potential-cycling is correlated with particle fragmentation leading to increased surface area.^{3,36,49} Our results suggest that reactive fracture of insulating Fe₂O₃ phases (**Fig. 4a**, **Fig. S13**) at temperatures greater than typical cycling temperatures is one potential strategy to reactivate Fe electrodes suffering from capacity fade related to the formation of large, insulating iron oxide domains.³⁶

The consistent presence of a dissolved ferrous species during the overall metal-forming reaction implies that accelerating oxide dissolution and increasing the solubility of the Fe²⁺ couple—via increased temperature, pH, or the addition of complexing agents—could increase the maximum rates of iron electrowinning and Fe electrodes charging, with possible tradeoffs in cycle life if implemented in secondary batteries. Most natural iron oxides are mined as large particles of dense Fe₂O₃, which are different from the morphologies showing the greatest activity for Fe electrowinning here (**Fig. 6**).³² New strategies for increasing the nanoscale porosity in oxide powders—including electrochemical milling as demonstrated here for *an*-Fe₂O₃—can enable the electrowinning of iron ores to metal in alkaline electrolytes at practical rates of reaction.

Conclusions

The electrochemical activity of hematite at $T < 100$ °C is substantially influenced by the nanoscale morphology of the reactant particle, with different α -Fe₂O₃ particles of consistent particle diameter proceeding through distinct reduction pathways to Fe metal. α -Fe₂O₃ particles with nanoscale pores follow a primarily dissolution–redeposition pathway leading to the formation of nanocrystalline Fe in the vicinity of partially reduced parent particles. On the other hand, annealed α -Fe₂O₃ particles with increased crystallinity were largely inert until particle fracture, presumably driven by (electro)mechanical stresses, which led to direct conversion of the oxide to metallic iron. The observation of rapid and complete reduction of annealed α -Fe₂O₃ particles to Fe

after electrochemically induced fracture provides a new strategy to activating naturally occurring iron oxide powders for decarbonized ironmaking.

Methods

Deionized water (DI H₂O) having a resistivity $\geq 18.1 \text{ M}\Omega\text{-cm}$ was obtained from a Millipore deionization system. $\alpha\text{-Fe}_2\text{O}_3$ (98%, metals basis) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%) were obtained from Thermo Scientific. Sodium hydroxide (NaOH, 50 wt.%) was obtained from Fisher Chemical. A naturally-occurring $\alpha\text{-Fe}_2\text{O}_3$ powder (*nat-Fe₂O₃*) was prepared by pulverizing a hematite specimen in a mortar and pestle selecting the -325 mesh fraction. $\alpha\text{-Fe}_2\text{O}_3$ particles were prepared following a previously reported procedure involving a sol-gel synthesis followed by annealing in a molten-salt flux.³⁹

Powder diffraction patterns of iron-oxide precursors were collected with a Bruker D2 phaser using a Cu-K α source (1.54 Å) with a step size of 0.02° and a $20\text{--}70^\circ$ 2θ range. Raman spectra were collected using a Renishaw Raman microscope equipped with a 1 mW 633 nm red laser as an excitation source and spectra were collected over 10 acquisitions. Microstructural analysis was performed by scanning electron microscopy (SEM, Thermo Fischer Apreo 2) using an accelerating voltage of 5–15 keV. Transmission electron microscopy (TEM) was performed on an FEI Titan 80-300 microscope at an accelerating voltage of 300 kV.

Thin films of $\alpha\text{-Fe}_2\text{O}_3$ were prepared by drop casting 12 mM (Fe basis) suspensions of particles in DI H₂O onto electrodes and dried for 7 min under heat from an infrared lamp. Particles were dispersed via horn sonication (SX Ultrasonics) and redispersed in a bath sonicator prior to drop casting. Samples for TEM were prepared by drop casting the same $\alpha\text{-Fe}_2\text{O}_3$ suspension onto a Cu/Au TEM grid (Ted Pella).

Slurries for battery-type electrodes were prepared by mixing α -Fe₂O₃ (70 wt.%), carbon black (Ketjenblack (17 wt.%), poly(tetrafluoroethylene) (PTFE) (10 wt.%), bismuth sulfide (Bi₂S₃) (3 wt.%) with ethanol. The slurry (6–8 mg cm⁻²) was applied to the Ni foam current collector (MTI Corporation, 1.6 mm), heated in a 5-ton hydraulic press for 30 s at 300 °C, and dried overnight at 80 °C under vacuum. Battery-type electrodes were cycled against a Ni foam counter and a Hg/HgO reference with 8 M KOH and 1 M LiOH and measured to be +974 mV vs RHE at room temperature.

A Thermo Fisher Scientific Helios 600 Nanolab dual beam FIB-SEM was used to prepare a cross-sectional sample from a fractured and intact *an*-Fe₂O₃ particle and thinned to electron transparency for further characterization. To avoid beam damage, carbon was deposited on the top of particle and while μ A currents were used to prepare cross sections, the face of the lamella was polished with pA currents. Although we cannot rule out the possibility of the milling process influencing the microstructure of the lamella, we observed a consistent SAED pattern between pc-Fe₂O₃ particles before and after FIB. Transmission Kikuchi diffraction (TKD) was performed on this sample using the Helios Hydra UX dual beam plasma focused ion beam/ scanning electron microscope (PFIB/SEM) equipped with an Oxford Symmetry S2 detector. For this purpose, a 30 kV accelerating voltage at 13 nA were used to generate Kikuchi patterns, which were subsequently analyzed using Oxford AztecCrystal software. A Themis Z 30-300 kV, Monochromated Aberration Corrected Transmission Electron Microscope operated at 300 kV was used for STEM and STEM-EDS on the cross-sectional FIB sample. Screen currents of 60 pA and 1 nA were used for HAADF-STEM imaging and STEM-EDS mapping, respectively. STEM-EDS maps were acquired at 512 X 512 resolution with a 20 μ s dwell time until a minimum of 100,000 counts were

collected for each element. Further image processing and analyses were conducted using the Velox software.

Nickel wire (600 Ni, Malin Co.) served as the counter electrode while a Hg/HgO electrode filled with 30 wt.% NaOH served as the reference and was measured at 0.926 V vs RHE at 80 °C. A rotating-ring-disk electrode assembly, with glassy-carbon serving as both the disk and ring electrodes, was controlled by a BlueRev RC-10k (BioLogic). All electrochemical experiments were conducted with a Biologic SP-200 potentiostat. A 35 mL polypropylene container (Nalgene) served as the electrochemical cell. NaOH solutions were diluted to 30 wt.% with DI H₂O and purged with N₂ for at least 30 min before experiments.

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Competing Interests

PAK, AK, and SWB have filed a patent have filed a patent on an electrochemical cell for producing iron metal from hematite.

Supporting Information Available

Preparation of *pc*-Fe₂O₃ and *an*-Fe₂O₃ particles, tables of thermodynamic parameters, tables of d-spacing values, tables of specific surface areas, additional SEM and TEM images, supporting discussion on dissolved species and mass transport limiting current density, supporting discussion on stresses generated prior to reactive fracture, and additional electrochemical characterization.

Associated Content

A pre-print of this manuscript is available: Shekhar, R., Mukhopadhyay, S., Sanchez, F., Konovalova, A., Boettcher, S.W., Devaraj, A., & Kempler, P.A. “Understanding the mechanism for the low-temperature reduction of Fe₂O₃ to Fe in alkaline electrolytes.” (2024). ChemRxiv. <https://doi.org/10.26434/chemrxiv-2024-dd895> (accessed August 1st, 2025).

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