Supplementary information for

Coupling Scrap Iron Valorization with Hydrogen Evolution via a Novel Iron Oxidation-to-Ferrate Electrochemistry

Linqing Fu [a], Jingsi Zhao [a], Yifei Yang [a], Long Lan [a], Hao Zhang [b], Tianyu Qiu [a], Jing Li [a], Yuliang Yuan [a], Wei Sun [a,*], Zhenye Kang [a], and Xinlong·Tian [a,*]

[a]*Key Laboratory of Agro-Forestry Environmental Processes and Ecological Regulation of Hainan Province, State Key Laboratory of Tropic Ocean Engineering Materials and Materials Evaluation, Hainan Provincial Key Lab of Fine Chem, School of Environmental Science and Engineering , Hainan University, 58 Renmin Road, Haikou 570228, P.R. China*

[b]*Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, P.R. China*

Corresponding E-mails:

weisun@hainanu.edu.cn (W. Sun); tianxl@hainanu.edu.cn (X. Tian)

Materials and Methods

Chemicals and materials:

Here, pure iron foils with a thickness of 0.1 mm were used as a substrate, with Fe content more than 99.99%, were purchased from Qinghe Runde Metal Materials Co., Ltd., China. Ti substrates NiFe LDH electrodes used in this paper were oxalic acid etched (Ti-e), the cut Ti foil was placed in 100 mL of near-saturated oxalic acid solution (wt% 30%) and reacted under micro-boiling conditions for 2 h until the solution changed to orange-yellow. Commercially available Raney nickel was used. Hydrochloric acid (HCl), ethanol (C_2H_5OH), potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium ferrate (VI), Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$), sulfuric acid (H_2SO_4), were all purchased from Macklin. The cation exchange membrane (CEM, DF2807A) was procured from Shandong Dongyue Polymer Material Co., Ltd., China, prior to use, the membrane were immersed in 0.02 $mol \cdot L^{-1}$ NaOH solution for at least 24 hours. The ultrapure water (18.25 MΩ cm) was prepared from the laboratory. All chemicals used in the experiments were of analytical grade and without any additional purification.

AF samples:

To ensure experimental controllability and minimize interference from extraneous factors, we selected artificially rusted iron as the scrap iron source in this study, we call them “AF”. Here, pure iron foils were cut to 5×8 cm and ultrasonically cleaned in ethanol to remove surface oils, followed by immersion in 0.1 $mol \cdot L^{-1}$ HCl for 6 hours to achieve sufficient surface etching and accelerate subsequent iron rusting. After rinsing off surface hydrochloric acid with deionized water, the iron foils were kept moist and placed in an electric thermostatic drying oven (60°C). Upon drying, the foils were re-wetted with deionized water and dried again. This wet-dry cycle was repeated multiple times. By varying the number of wetting cycles and water volume, four distinct rust grades were obtained: AF 1, AF 2, AF 3, and AF 4. For AF 1, the preprocessed iron foil was just surface-wetted, placed horizontally in a water-free vessel, and subjected to ten wet-dry cycles, until there is no significant change on the surface. AF 2 was prepared similarly to AF 1 but with a reduced number of wet-dry cycles to five. For AF 3, the preprocessed iron foil was horizontally positioned in a water-containing vessel with the water level precisely flush with the foil surface, forming a ~1 mm thick water film, and subjected to ten wet-dry cycles. And for AF 4, the preprocessed iron foil was fully immersed in a large volume of water (approximately 200 mL). After complete evaporation, fresh water was added, and this wet-dry cycle was repeated ten times. All aqueous phases referenced above—including rinsing, wetting, immersion, and solution preparation—utilized ultrapure water.

NiFe-LDH catalyst:

The Ti-e substrate was cut into appropriate sizes. NiFe layered double hydroxide (LDH) electrodes were then fabricated on Ti-e via electrodeposition. Specifically, the cut Ti-e was immersed in a mixed solution containing $FeSO_4 \cdot 7H_2O$ and $NiSO_4$ with a Ni:Fe molar ratio of 3:1. Electrodeposition was performed at a constant potential of −1 V (vs. Ag/AgCl) until a total charge of 1 C was passed, resulting in the formation of NiFe LDH on Ti-e. Finally, the electrode was thoroughly rinsed with ultrapure water and dried at room temperature for subsequent use.

$Fe(OH)_3$/Fe samples:

The Fe foil was cut into appropriate sizes and ultrasonically cleaned in ethanol for 2 min. Surface oxide layers were subsequently removed using 0.1 mol L^{-1} HCl immersed for 20 min. The pretreated Fe foil was then immersed in a solution containing 0.1 mol L^{-1} $FeCl_3$. Electrodeposition was carried out at a constant potential of −1 V (vs. Ag/AgCl) until a total charge of 1 C was passed. After rinsing thoroughly with ultrapure water, the sample was annealed in a muffle furnace at 200 °C for 2 h or 400 °C for 4 h in air, resulting in the final $Fe(OH)_3$/Fe-200 and $Fe(OH)_3$/Fe-400 samples.

Experimental Section

In this work, since ferrate(VI) solutions exhibit a characteristic purple color, UV-Vis spectrophotometry is employed for quantitative analysis. Initially, as show in fig. S1a, we performed wavelength scanning (400–1000 nm) of 1-5 $mmol \cdot L^{-1}$ K_2FeO_4 AR in 6 $mol \cdot L^{-1}$ KOH solution, identifying its optimal absorption wavelength at 502 nm. Consequently, all subsequent measurements were conducted at 502 nm. As show in fig. S1b, a standard curve correlating absorbance with concentration was established by preparing a series of K_2FeO_4 solutions at known concentrations. This enables determination of unknown K_2FeO_4 concentrations for subsequent calculations.

Yield rate calculation:

The yield rate ($mmol \cdot L^{-1} \cdot h^{-1} \cdot cm^{-2}$) of products was calculated using the following equation:

$$\text{Yield rate} = \frac{C}{St} \times 100\% \tag{S1}$$

Where "C" is the K_2FeO_4 concentration determined by UV-Vis spectrophotometry, $mmol \cdot L^{-1}$; "t" represents the reaction time, h; and "S" stands for the active surface area of the anode involved in the reaction, cm^2.

Faraday efficiency calculation：

The Faraday efficiency equation was utilized to evaluate current utilization efficiency during electrolysis.

According to the Faraday efficiency equation:

$$FE = \frac{mnF}{Q} \times 100\% \tag{S2}$$

Where "m" is the molar mass of the ferrate product, $g \cdot mol^{-1}$; "n" represents the number of electrons transferred per ferrate synthesized from anode materials, in this work, for AF, we used n=3, for Fe foil n=6, for H_2 n=2; the "F" is the Faraday's constant, 96485 $C \cdot mol^{-1}$; "Q" is the total charge transferred during the reaction, C, and:

$$Q = \int Idt \tag{S3}$$

Where "t" represents the electrolysis duration, s; and "I" denotes the real-time current magnitude, A.

Hydrogen collection method and molar quantity calculation:

Hydrogen gas was collected using the water displacement method, with the collection setup illustrated in Figure S14. In the cathode cell, the Faraday efficiency is also employed to evaluate current utilization efficiency for hydrogen generation, the number of electrons transferred is two.

In the Faraday efficiency formula, "n"(molar quantity) for hydrogen is calculated as follows:

According to the ideal gas equation of state:

$$n = \frac{pV}{RT} \tag{S4}$$

Where the “R” is the gas constant (8.314 J·mol^{-1}·K^{-1}), “T” is the ambient temperature, 303.15 K (30 °C), “p” denotes the partial pressure of hydrogen gas, pa; and “V” represents the volume of gas measured by the water displacement method, ml.

In the experimental setup for water displacement:

$$p_{H_2O} + p_{gas} = p_{atm} \tag{S5}$$

And:

$$p_{H_2O} = \rho_{H_2O} gh\triangle \tag{S6}$$

Where “ρ_{H_2O}” is the water density, 1 kg˙m^3; “g”, 9.8 N˙kg^{-1}, and “h△” denotes the water level difference between the interior and exterior of the apparatus, m. “p_{gas}” represents the total gas pressure inside the apparatus, which includes contributions from both hydrogen and water vapor. Therefore, the saturated vapor pressure of water must be subtracted during calculations. At ambient temperature 303.15 K, the saturated vapor pressure of water is 0.04 atm. And “p_{atm}” is the ambient atmospheric pressure, 1.013×10^5 pa.

In summary, the amount of substance hydrogen (n_{H_2}) collected via water displacement method at 303.15 K is calculated as:

$$nH2 = \frac{[(1 - 0.04)\ patm\ -\ \rho H2Ogh\triangle\ ]V}{RT} \tag{S7}$$

Electrochemical measurements：

Electrochemical tests were performed in a three-electrode system using CHI760E in 6 M KOH solution. The prepared samples with 1 cm^2 size were used as working electrodes and a platinum foil with 1 cm^2 size, and the standard Hg/HgO electrode was used as reference and counter electrodes, respectively. The solution resistances were determined by the electrochemical impedance spectroscopy (EIS) method. EIS measurements were obtained over a frequency range from 100 kHz to 0.1 Hz. Potentials were calibrated relative to the reversible hydrogen electrode (RHE) potentials with iRcompensation(R-solution resistance): E (vs. RHE) = E (vs. Hg/HgO) + 0.0592*pH+0.098-IR.

The overall water splitting performance was evaluated in a two-electrode system using CHI760E in 6 M KOH solution. The cathodes area were 0.5 cm^2 and the anode was 15 cm^2. The activity with iRcorrected was investigated by linear sweep voltammetry (LSV) with a low scan rate of 5 mV s^{-1}.

Material characterizations:

The bulk and surface crystal structure of AF samples are investigated by X-ray diffraction (XRD), respectively, which equipped with a D/max2550 V apparatus and a CuKα radiation source (λ = 1.5406) with a data recording range of 10–80◦and a step size of 0.02◦.The surface compositions and elements‘ valence states were determined by X-ray photoelectron spectroscopy (XPS) with an instrument of ESCALAB 250Xi, which an energy step size of 0.05 eV to obtain high-resolution XPS spectra. All deconvoluted high-resolution XPS spectra were calibrated by C-1s at 284.8 eV. Scanning electron microscopy (SEM) was used to examine the morphology with an instrument of QuattroS. In situ FTIR measurements were conducted using an electrochemical workstation equipped with an H-cell and an IRTracer-100 spectrometer. The self-made AF 4 served as the working electrode in 6 M KOH solution. All spectra were collected with a resolution of 8 cm^{-1}. The in situ test was performed at a potential of 1 V(vs. Hg/HgO) for a duration of 1 h and recorded every 10 minutes during the period.

Supplementary Figures

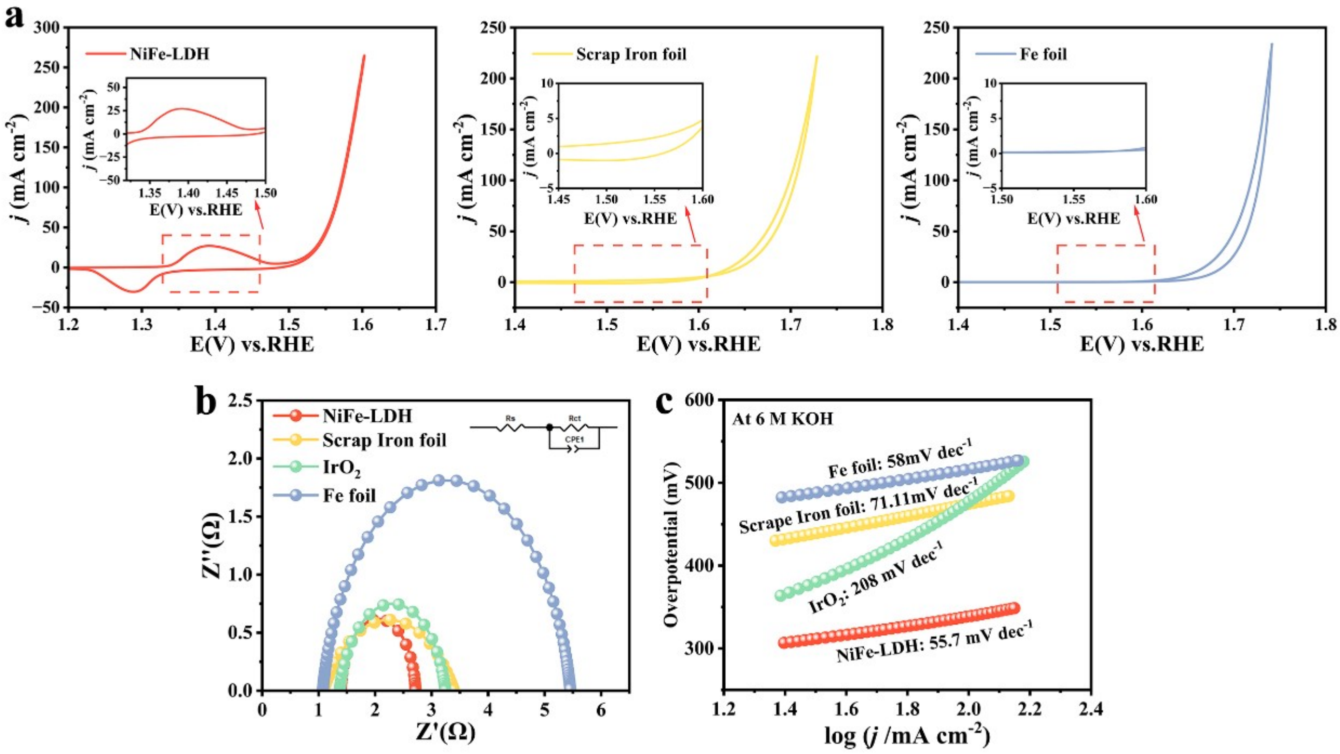
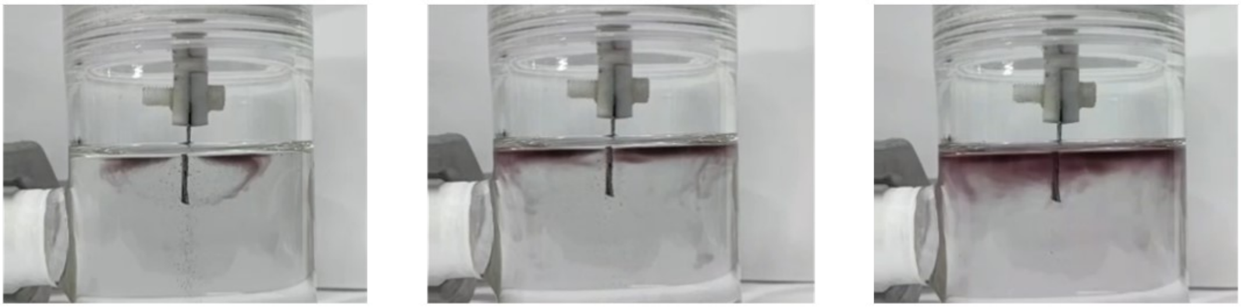


Figure S1 (a) LSV polarization curves of different anode materials. (b) Nyquist plots from EIS measurements of prepared different materials at 0.7 V (vs. Hg/HgO). (c) The corresponding Tafel plots, the obtained slopes are labeled accordingly in the figure. The electrodes area is fixed at 0.5 cm^2 for all materials. All the electrolyte is the 6 M KOH.



1 min 4 min 8 min

Figure S2. Time-lapse photographs showing the evolution of the anolyte over 10 minutes under a constant current density of 10 mA cm^{-2}, the electrolyte is the 6 M KOH.

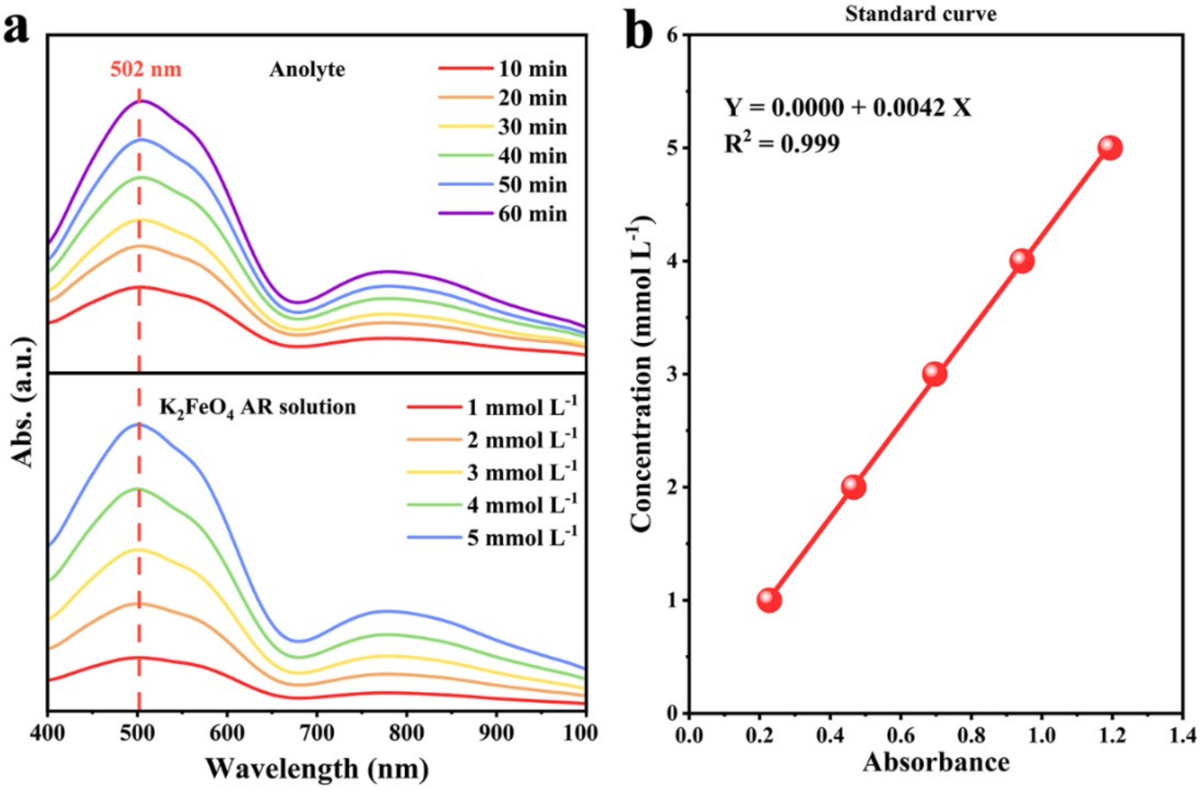


Figure S3. (a) Absorption spectra comparison chart of K_2FeO_4 AR solutions at different concentrations and anolyte at different electrolytic time in 6 M KOH. (b) Standard curve for K_2FeO_4 solution in 6 M KOH.

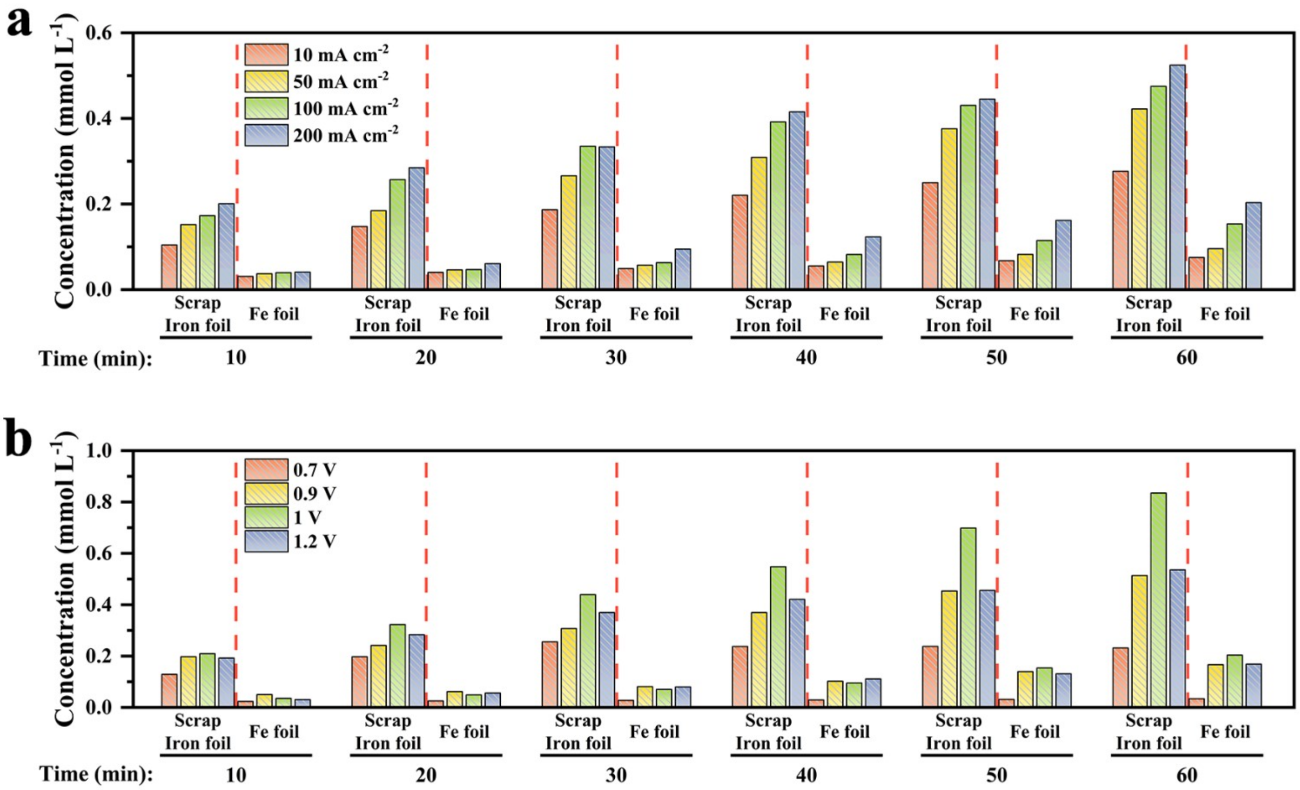


Figure S4. (a) Temporal evolution of potassium ferrate concentration in the anolyte recorded at 10-min intervals for both scrap iron foil and pure Fe foil under different current densities. (b) Temporal evolution of potassium ferrate concentration in the anolyte recorded at 10-min intervals for both scrap iron foil and pure Fe foil at different applied potentials (vs. Hg/HgO). All the electrolyte is 6 M KOH.

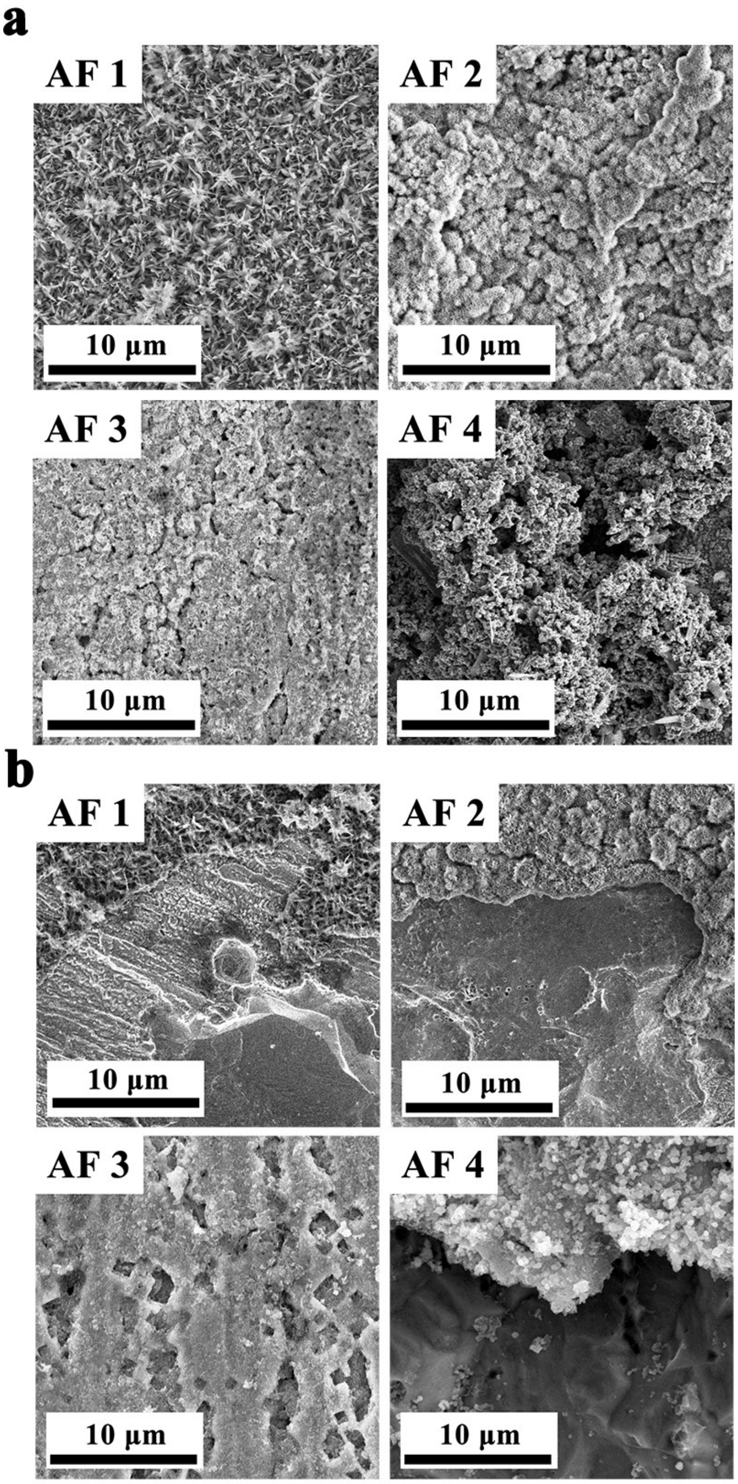


Figure S5. SEM image of AF 1 to AF 4, (a) before and (b) after 1 h electrolysis in 6 M KOH.

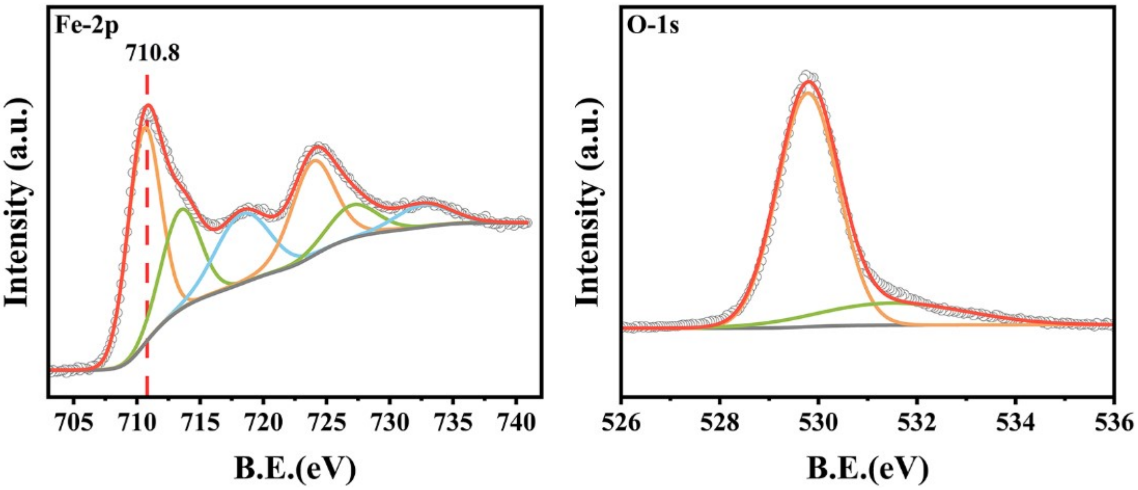
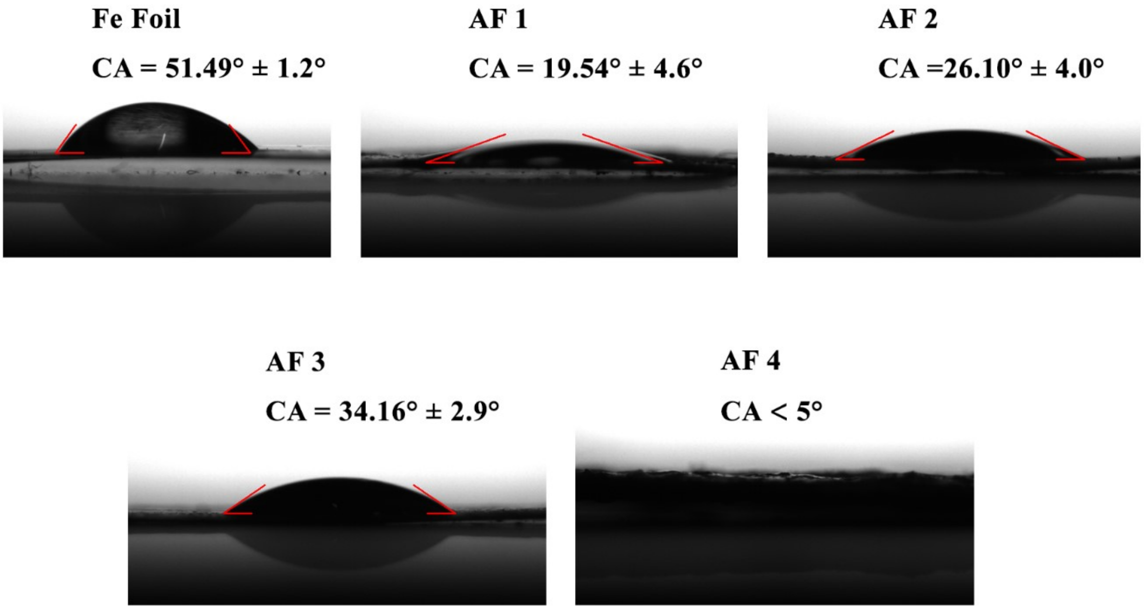


Figure S6. XPS of α-Fe_2O_3.



Fe Foil

CA = 51.49° ± 1.2°

AF 1

CA = 19.54° ± 4.6°

AF 2

CA =26.10° ± 4.0°

AF 3

CA = 34.16° ± 2.9°

AF 4

CA < 5°

Figure S7. Water contact angle of Fe foil and AF 1 to AF 4.

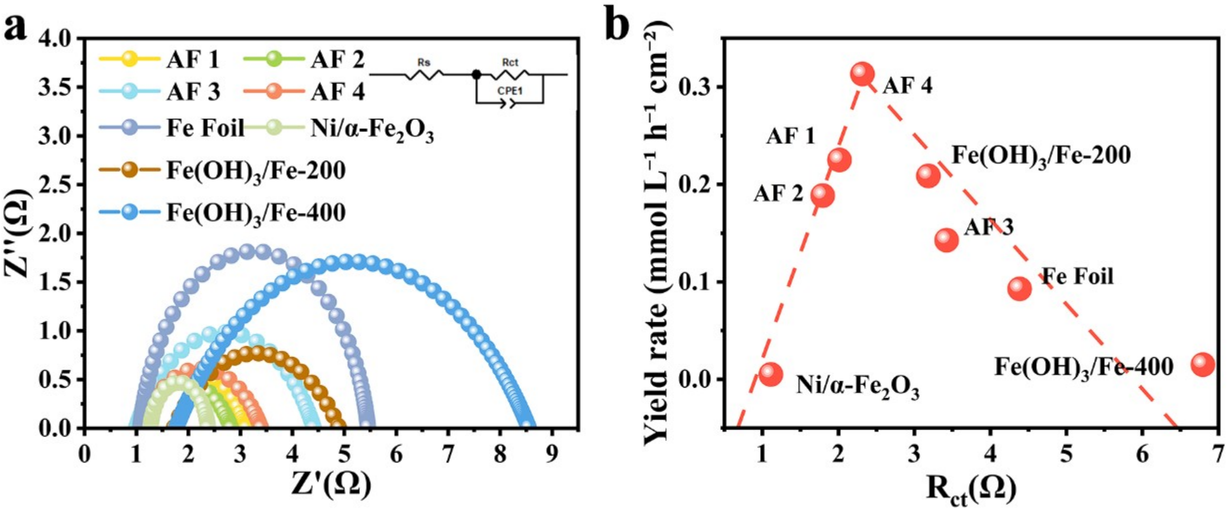


Figure S8. (a) EIS Nyquist plots of different materials at 0.7V (vs. Hg/HgO). (b) Volcano-type correlation between Rct and FeO_4^{2-} yield rate for the different materials at 10 mA cm^{-2} and 10 min condition. The electrolyte is the 6 M KOH with O_2-saturated. Raney nickel with 0.5 cm^2 is served as the counter electrode.

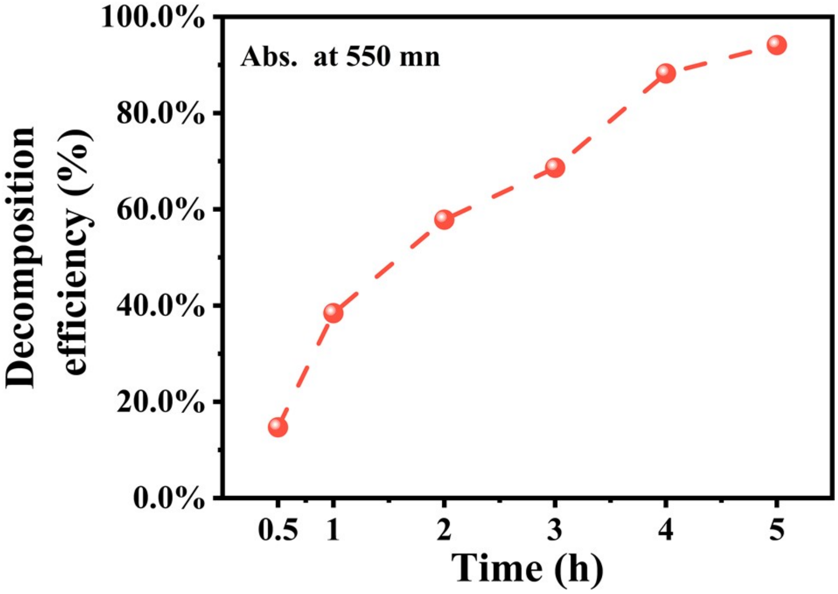


Figure S9. Degradation efficiency of MB treated with anolyte containing FeO_4^{2-}.

Figure S10. Photographs corresponding to the degradation process of MB and all solutions were diluted five-fold.

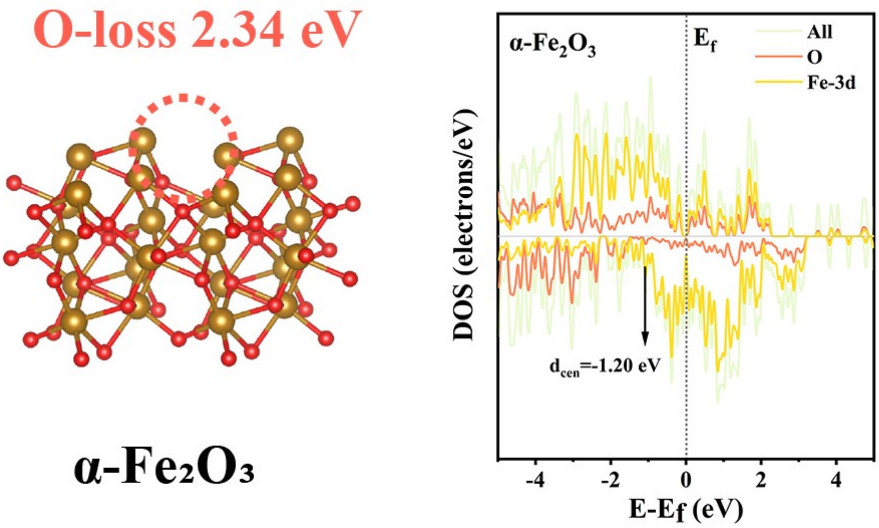


Figure S11. Oxygen loss energy of the α-Fe_2O_3.

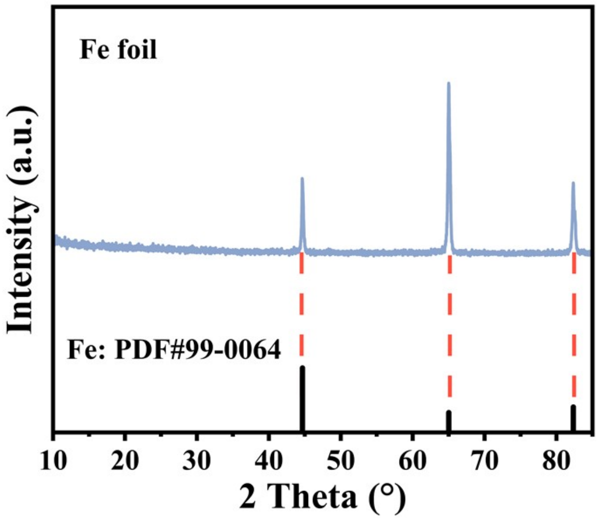


Figure S12. XRD of pure Fe foil.

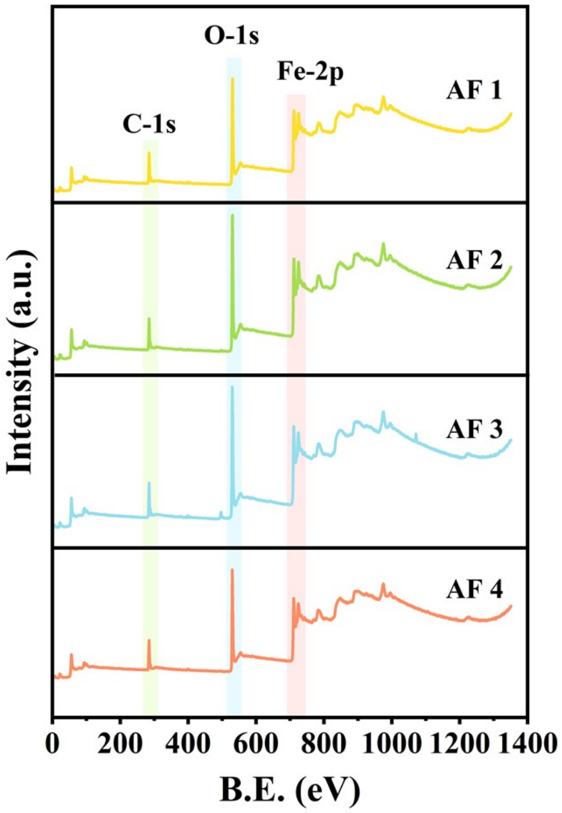


Figure S13. XPS Full-spectra of AF 1 to AF 4.

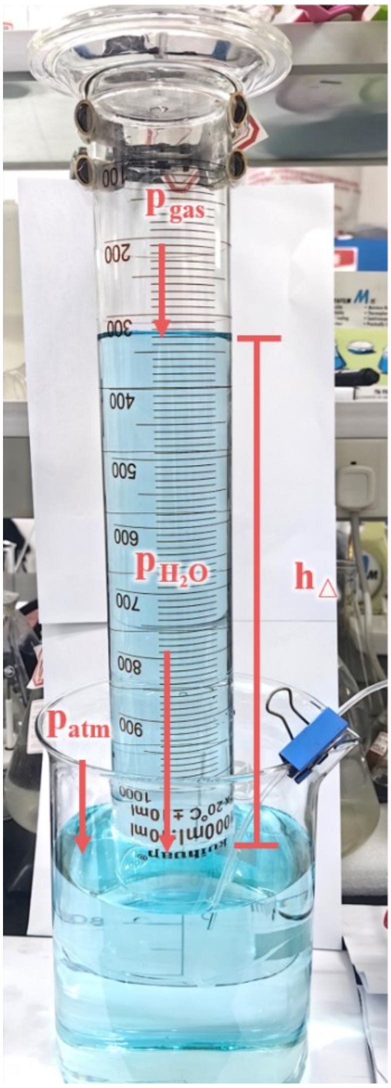


Figure S14. Hydrogen collection system. The liquid in the container is ultrapure water with H_2-saturated. For clear visualization, the ultrapure water in the container is dyed with MB.

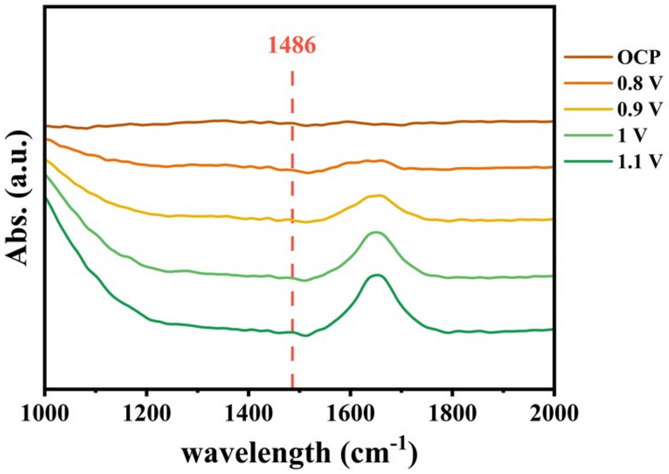


Figure S15. In situ FTIR spectra of pure Fe foil at various potentials.

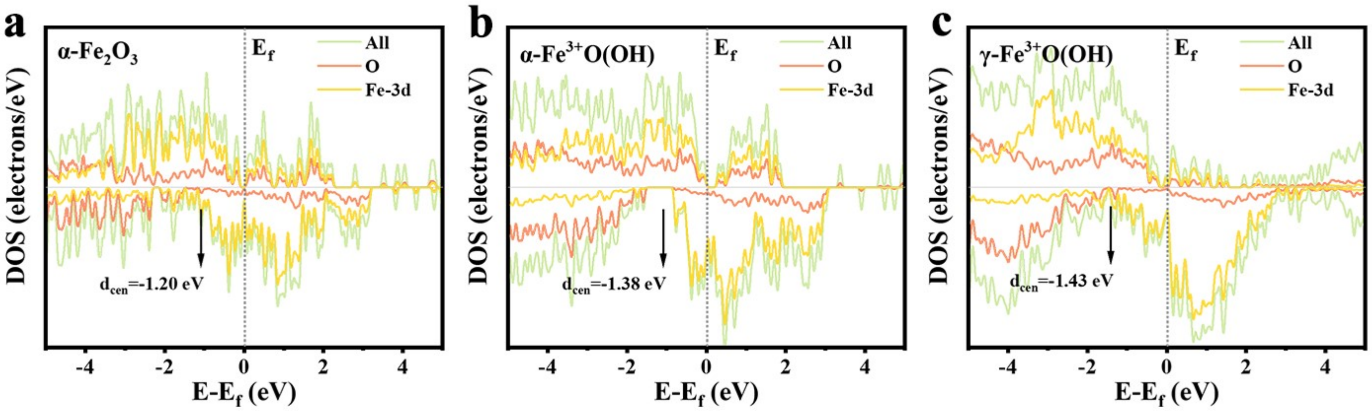


Figure S16. (a)-(c) The DOS profiles for three iron oxides.