

# **Supporting Information**

## **Galena oxidation in oxygen-bearing acidic solutions**

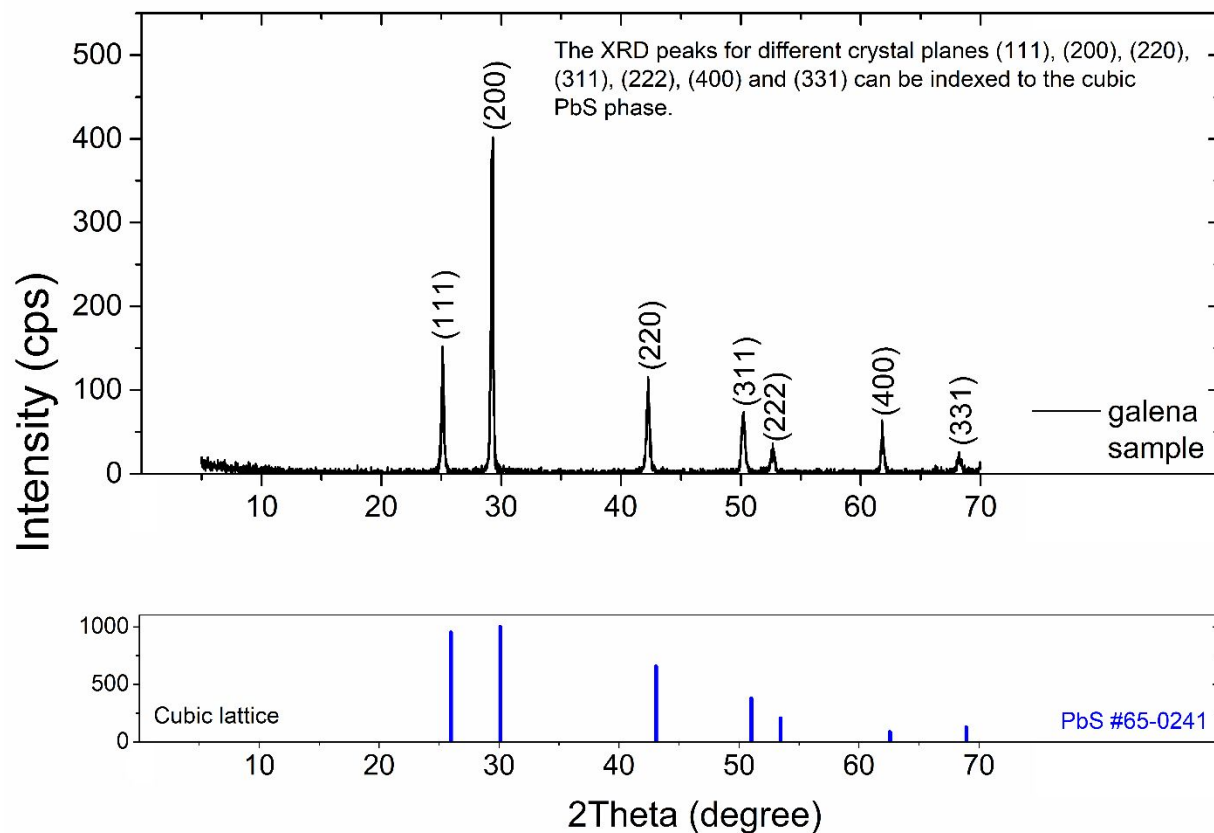
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## X-ray diffraction analysis

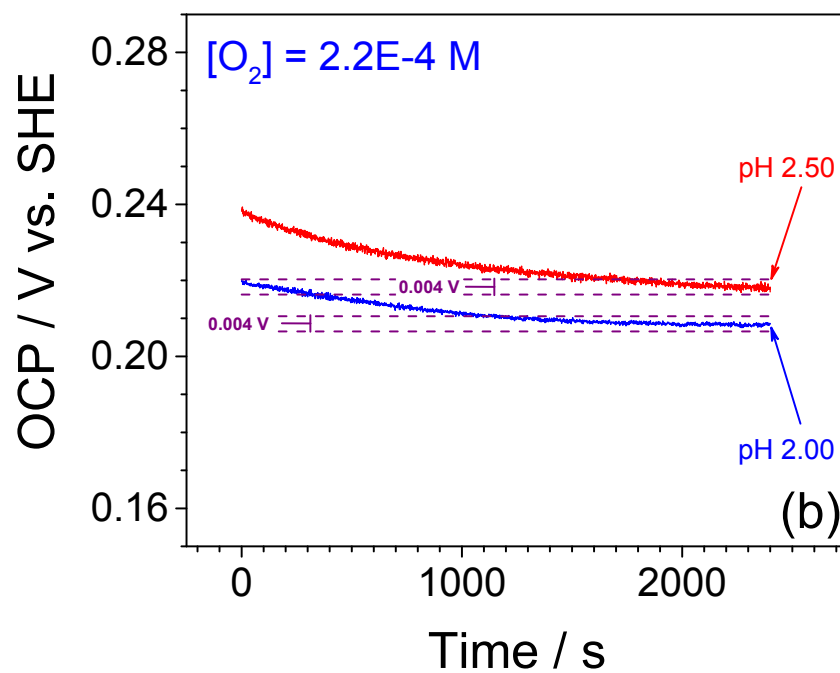
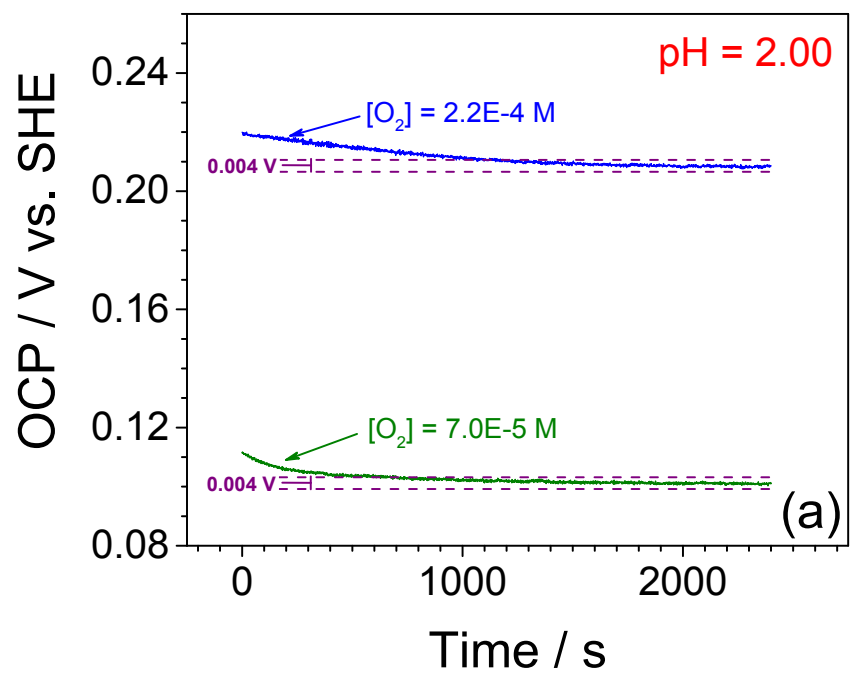


**Figure S1.** The X-ray diffraction pattern of the galena sample.

X-ray diffraction (XRD) analysis was carried out with Cu target tube (voltage = 30.0 kV; current = 30.0 mA). The XRD diagram was recorded in the range 2Theta = 5° - 70°.

## Open circuit potential (OCP) versus time

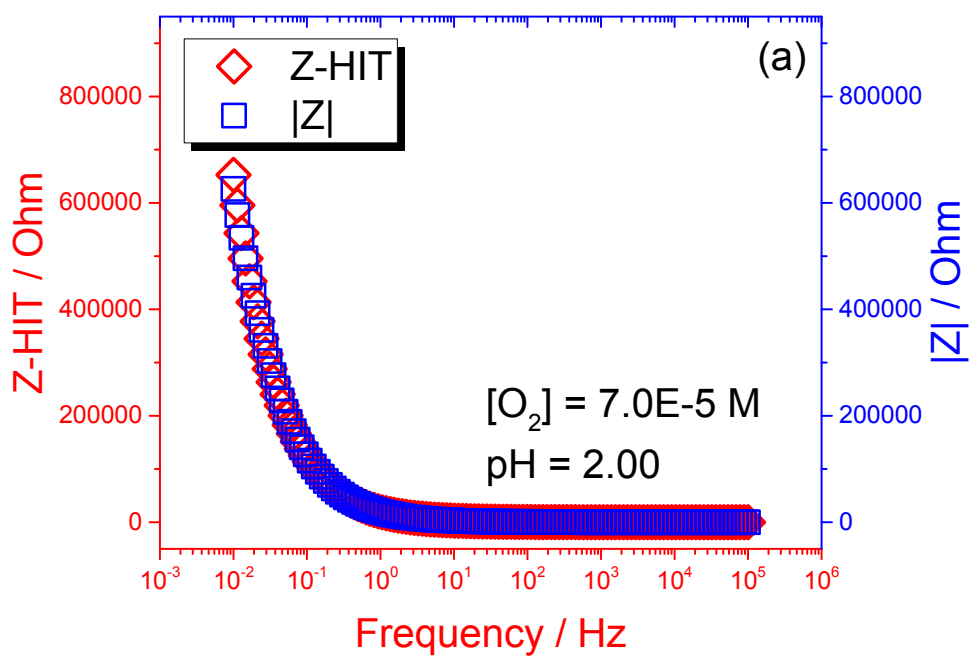
The OCP was considered stable when the drift of the measured potential was below 4 mV for at least 10 min (Fig. S2).

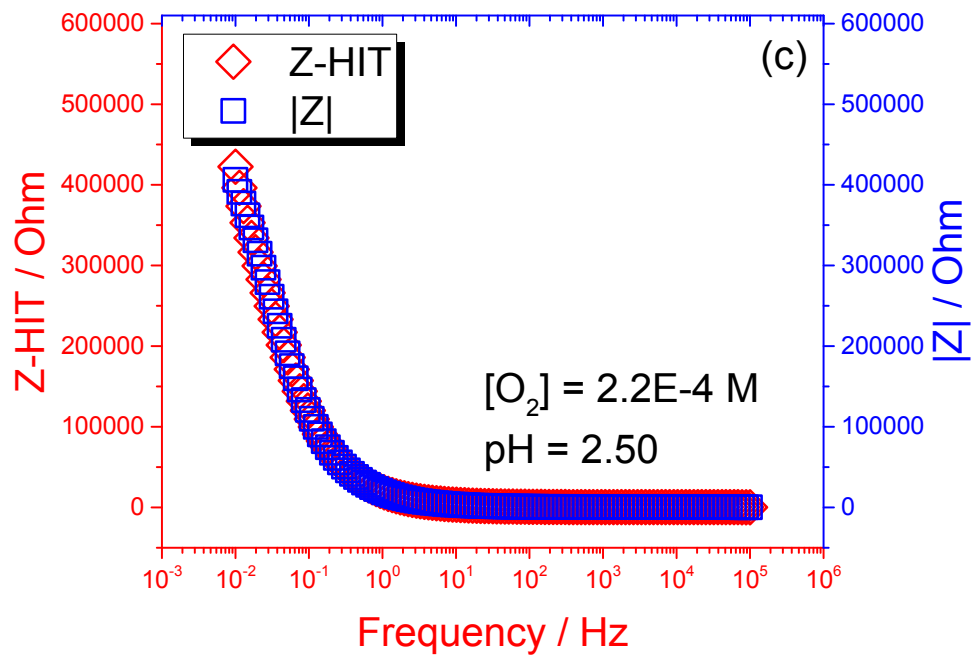
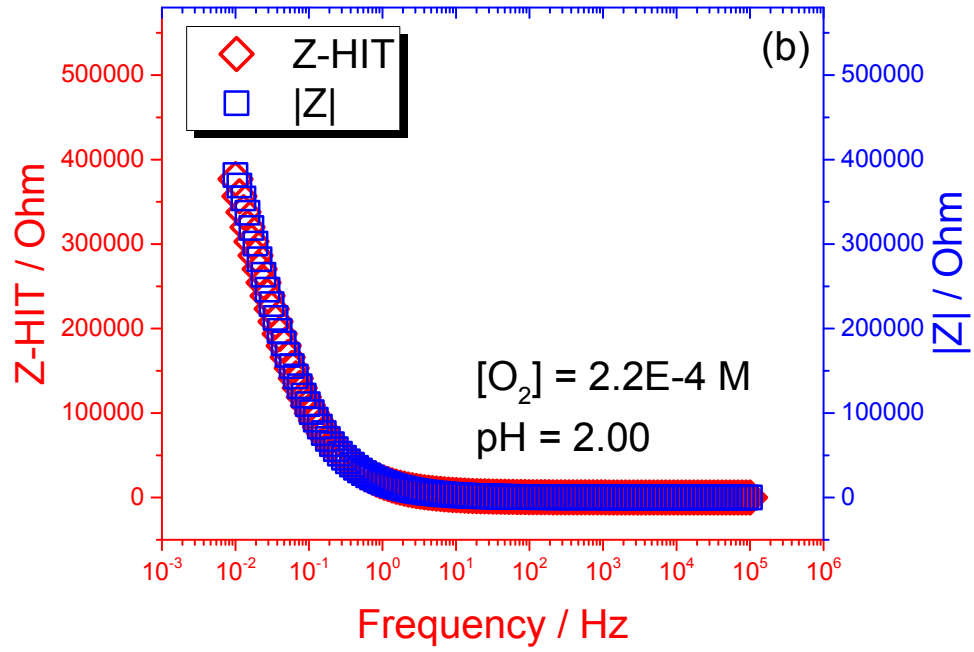


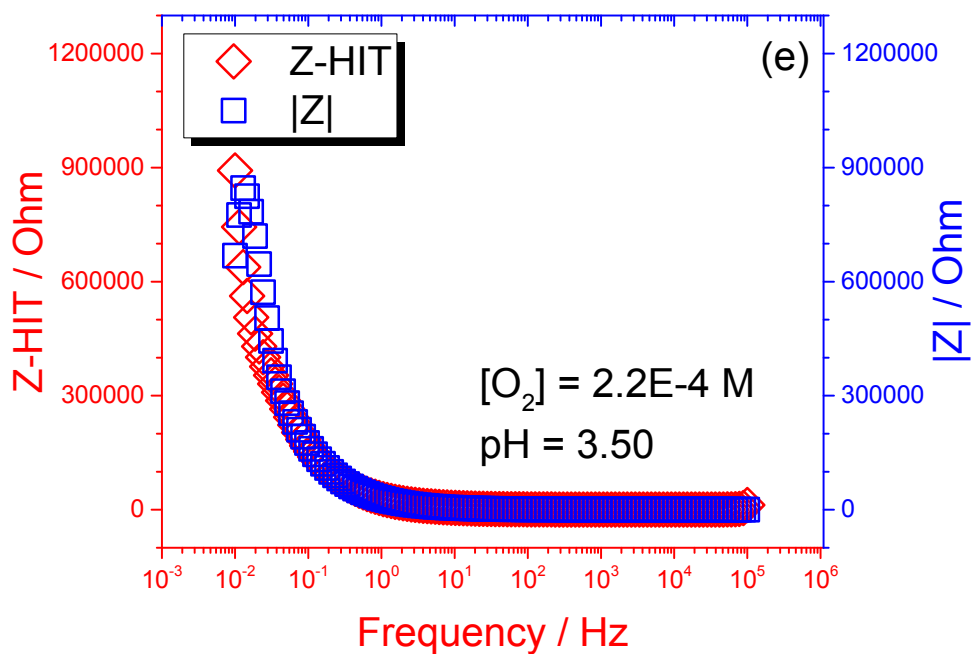
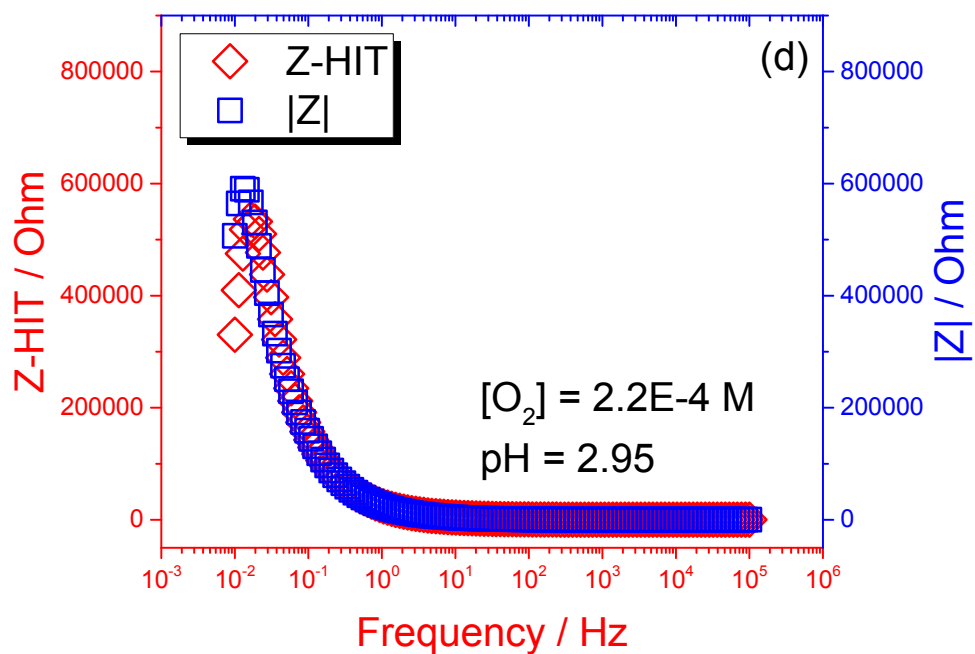
**Figure S2.** The variation of the OCP versus time at 25°C. (a) pH 2.00 and two different oxygen concentrations ( $[O_2]$ ) and, respectively, (b)  $[O_2] = 2.2E-4$  and two different pH values.

## Hilbert transform

The Hilbert transform (Z-HIT)<sup>1</sup> can be used to establish the validity of impedance data set. In this order, Z-HIT transform was carried out over the measurement frequencies (10 mHz - 100 kHz). Figs. S3(a-e) present the Hilbert transforms (Z-HIT) in comparison with the experimental data ( $|Z|$ ). Even if at low frequencies, there are small differences between Z-HIT and  $|Z|$  (Figs. S3(d and e)), the perfect concordance between the two parameters at the other frequencies shows that the experimental data set can be considered valid.<sup>2</sup>







**Figure S3.** Z-HIT tests for the identification of EIS artifacts produced by time drift (at low frequencies) and mutual induction (at high frequencies) at 25°C. (a)  $[O_2] = 7.0E-5$  and pH = 2.00; (b)  $[O_2] = 2.2E-4$  and pH = 2.00; (c)  $[O_2] = 2.2E-4$  and pH = 2.50; (d)  $[O_2] = 2.2E-4$  and pH = 2.95 and, respectively, (e)  $[O_2] = 2.2E-4$  and

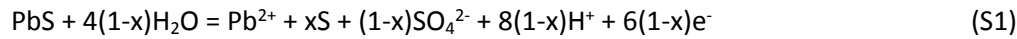
pH = 3.50. The Z-HIT curves (red  $\diamond$ ) should match the impedance modulus data (blue  $\square$ ). At intermediate and high frequencies (Figs. S3a-e), there are no differences between the experimental data and Z-HIT curves, eliminating the existence of any parasitic effect caused by the magnetic field produced by the current passing through the cables. There are only minor differences at low frequencies (suggesting possible small differences between the initial and final states of the system during the impedance measurements, differences possibly caused by reactions like dissolution, precipitation, adsorption etc.) for spectra recorded at pH 2.95 (d) and 3.50 (e). The experimental conditions are presented in each graph.

### Theoretical expression for the mixed potential (oxidation potential) and current density of aqueous oxidation of galena

A theoretical expression of  $j_{ox}$  can be obtained following a procedure like that of Holmes and Crundwell<sup>3</sup> or Badica and Chirita<sup>4</sup> and considering that charge transfer coefficients are not necessarily equal with 0.5.<sup>5</sup>

The half reactions are:

- anodic oxidation of galena



with the corresponding current density

$$j_{PbS} = k_{PbS} [H^+]^{\beta} \exp\left(\frac{\alpha_{PbS} FE}{RT}\right) \quad (S2)$$

- cathodic reduction of oxygen

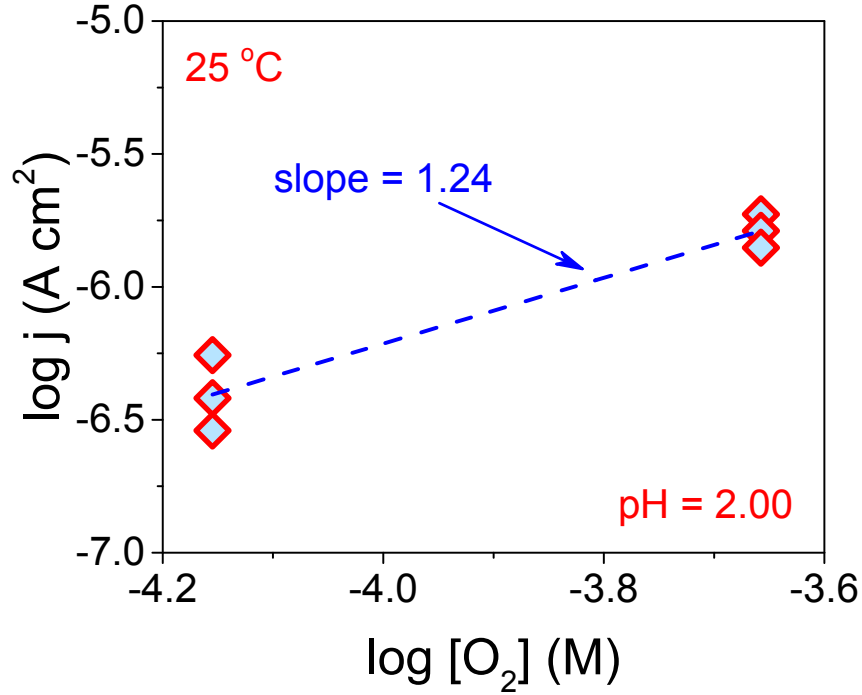


with the corresponding current density

$$j_{O_2} = -k_{O_2} [H^+]^{\gamma} [O_2]^{1.24} \exp\left(\frac{-(1-\alpha_{O_2}) FE}{RT}\right) \quad (S4)$$

E is the potential, F is the Faraday constant, R is the gas constant, T is the absolute temperature,  $\beta$  and  $\gamma$  are the exponents of  $[H^+]$ ,  $k_{PbS}$  and  $k_{O_2}$  are the rate constants, and  $\alpha_{PbS}$  and  $\alpha_{O_2}$  are the corresponding charge transfer coefficients. 1.24 is the slope of  $\log j$  versus  $\log [O_2]$  plot (Figure S4), determined in

conformity with the procedure described by Badica and Chirita.<sup>4</sup>  $j$  is the current density registered at a cathodic overpotential of 0.19 V with respect to  $E_{ox}$  at the two concentrations of  $O_2$ .



**Figure S4.**  $\log j$  versus  $\log [O_2]$  in the experiments performed at pH 2. The cathodic  $j$  values were obtained at overpotentials of 0.19 V with respect  $E_{ox}$ .

At oxidation potential,  $E_{ox}$ ,

$$j_{PbS} = -j_{O_2} \quad (S5)$$

Following procedure described by Holmes and Crundwell<sup>3</sup> or Badica and Chirita<sup>4</sup> one obtains:

$$E_{ox} = \frac{RT}{(1 + \alpha_{PbS} - \alpha_{O_2})F} \ln \left( \frac{k_{O_2}}{k_{PbS}} [H^+]^{(\gamma - \beta)} [O_2]^{1.24} \right) \quad (S6a)$$

$$E_{ox} = \frac{0.059}{1 + \alpha_{PbS} - \alpha_{O_2}} \log \left( \frac{k_{O_2}}{k_{PbS}} [H^+]^{(\gamma - \beta)} [O_2]^{1.24} \right) \quad (S6b)$$

As  $j_{ox} = j_{PbS}$  it results that:

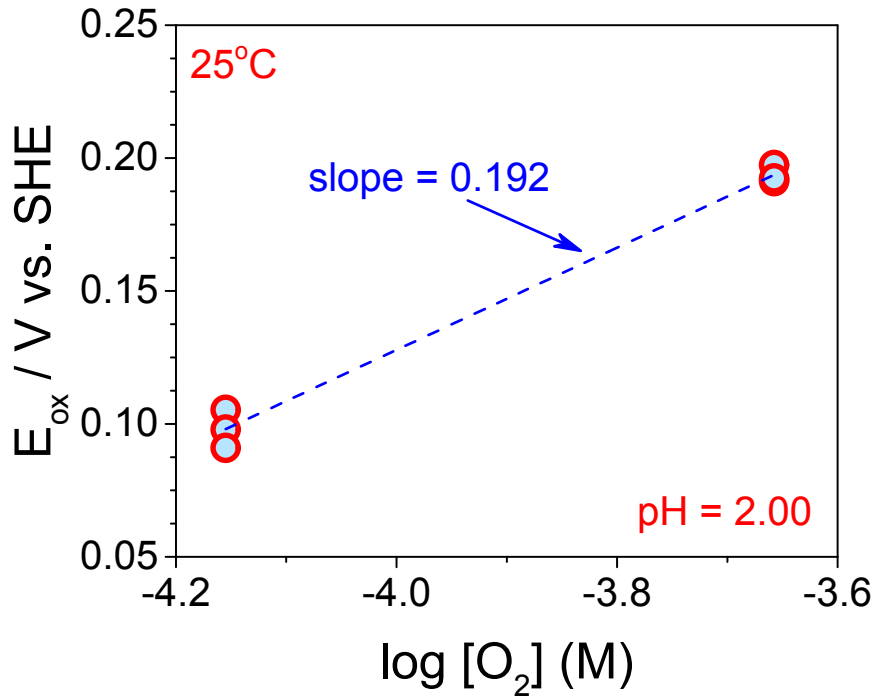


$$j_{ox} = k_{pbs} [H^+]^{\beta} \exp\left(\frac{\alpha_{pbs} F E_{ox}}{RT}\right) \quad (S7)$$

Inserting Eq. S6a in Eq. S7 one obtains:

$$j_{ox} = k_{pbs} \left( \frac{k_{O_2}}{k_{pbs}} \right)^{\frac{\alpha_{pbs}}{1 + \alpha_{pbs} - \alpha_{O_2}}} [O_2]^{\frac{1.24 \alpha_{pbs}}{1 + \alpha_{pbs} - \alpha_{O_2}}} [H^+]^{\frac{(\gamma - \beta) \alpha_{pbs}}{1 + \alpha_{pbs} - \alpha_{O_2}} + \beta} \quad (S8)$$

$\alpha_{pbs}$  and  $\alpha_{O_2}$  can be obtained from the slopes of  $E_{ox}$  versus  $\log [O_2]$  (i.e., 0.192) (Figure S5) and  $\log j_{ox}$  versus  $\log [O_2]$  (i.e., 0.96) (see Figure 8 in the article).



**Figure S5.**  $E_{ox}$  versus  $\log [O_2]$  in the experiments performed at pH 2.

$$\frac{1.24 \cdot 0.059}{1 + \alpha_{pbs} - \alpha_{O_2}} = 0.192 \quad (S9)$$

$$\frac{1.24 \alpha_{pbs}}{1 + \alpha_{pbs} - \alpha_{O_2}} = 0.96 \quad (S10)$$

$$1 + \alpha_{pbs} - \alpha_{O_2} = 0.381 \quad (S11)$$

$$\alpha_{PbS} = 0.295 \quad (S12)$$

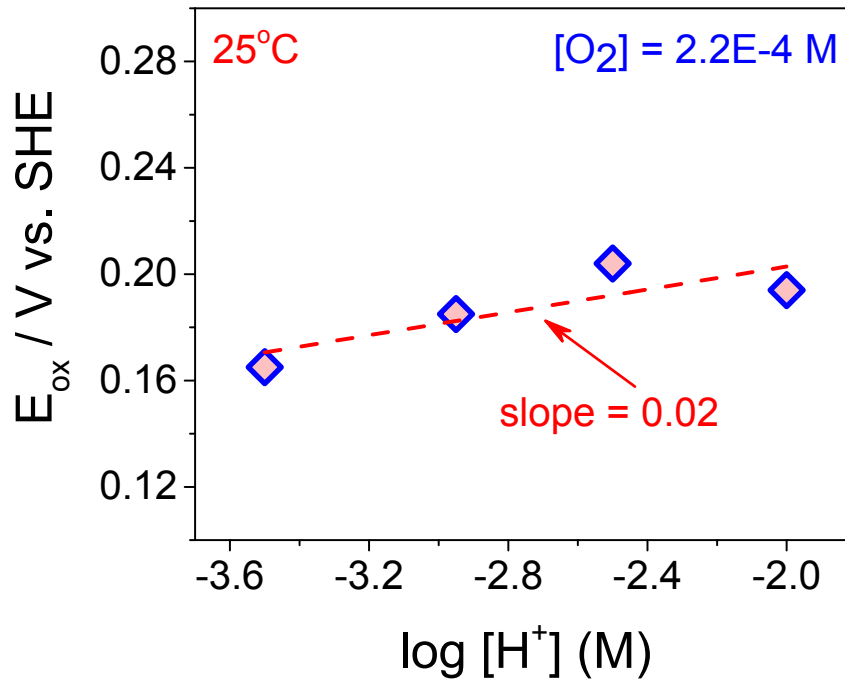
$$\alpha_{O_2} = 0.914 \quad (S13)$$

From  $E_{ox}$  versus  $\log [H^+]$  plot (Figure S6) we can compute  $\gamma - \beta$  value.  $\gamma - \beta = 0.13$ .  $\beta$  can be obtained from the slope of  $\log j_{ox}$  versus  $\log [H^+]$  (i.e. -0.02) (see Figure S7).  $\beta$  is -0.12. It results that  $\gamma=0.01$ .

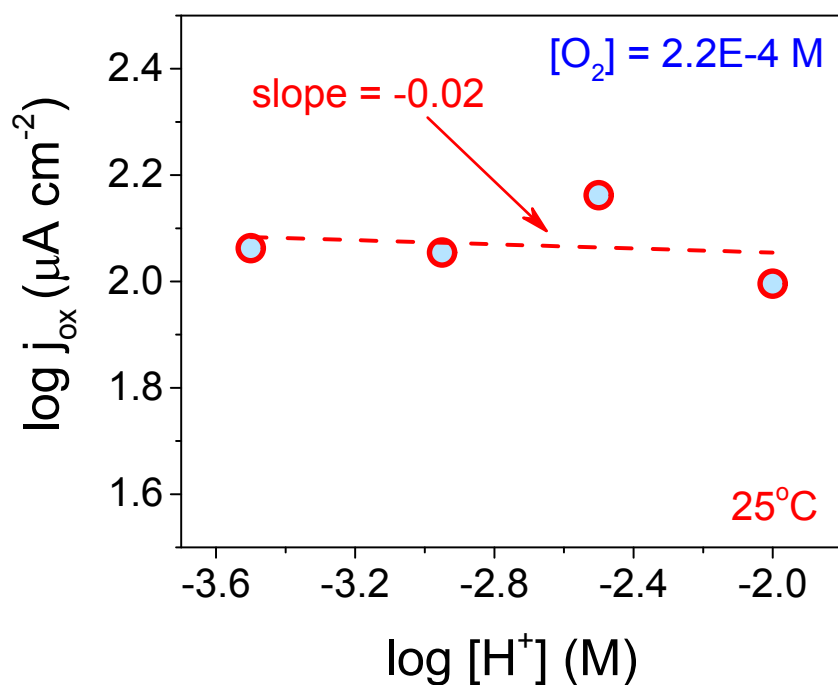
In consequence,

$$j_{ox} = k_{PbS} \left( \frac{k_{O_2}}{k_{PbS}} \right)^{0.77} [O_2]^{0.96} [H^+]^{-0.02} \quad (S14)$$

an equation similar to Eq. (5) in the article, with  $k = k_{PbS} \left( \frac{k_{O_2}}{k_{PbS}} \right)^{0.77}$ .



**Figure S6.**  $E_{ox}$  versus pH in the experiments performed at  $[O_2]=2.2E-4$  M.



**Figure S7.**  $\log j_{ox}$  versus  $\log [H^+]$  in the experiments conducted at  $[O_2]=2.2e-4 M$ .

## References

- (1) Schiller, C.A.; Richter, F.; Gulzow, E.; Wagner, N. Validation and evaluation of electrochemical impedance spectra of systems with states that change with time. *Phys. Chem. Chem. Phys.* **2001**, *3*, 374-378.
- (2) Ehm, W.; Gohr, H.; Kaus, R.; Roseler, B.; Schiller, C. A. The evaluation of electrochemical impedance spectra using a modified logarithmic Hilbert transform. *ACH Mod. Chem.* **2000**, *137*, 145-158.
- (3) Holmes P.R.; Crundwell, F.K. The kinetics of the oxidation of pyrite by ferric ions and dissolved oxygen: an electrochemical study. *Geochim. Cosmochim. Acta* **2000**, *64*, 263-274.
- (4) Badica, C.E.; Chirita, P. An electrochemical study of the oxidative dissolution of iron monosulfide (FeS) in air-equilibrated solutions. *Electrochim. Acta* **2015**, *178*, 786-796.
- (5) Chirita, P.; Schlegel, M.L. Pyrite oxidation in air-equilibrated solutions: An electrochemical study, *Chem. Geol.* **2017**, *470*, 67-74.