# Spontaneous Water Oxidation at Hematite (α-Fe$_2$O$_3$) Crystal Faces

*S. Chatman[1*†], P. Zarzycki[2], and K. M. Rosso[1,*]*

[1]Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Washington, USA

[2]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

**Corresponding Author**

*Kevin M Rosso: Kevin.Rosso@pnnl.gov

*Shawn Chatman: chatmans@caltech.edu

**Present Address**
[†] Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA  91125 USA
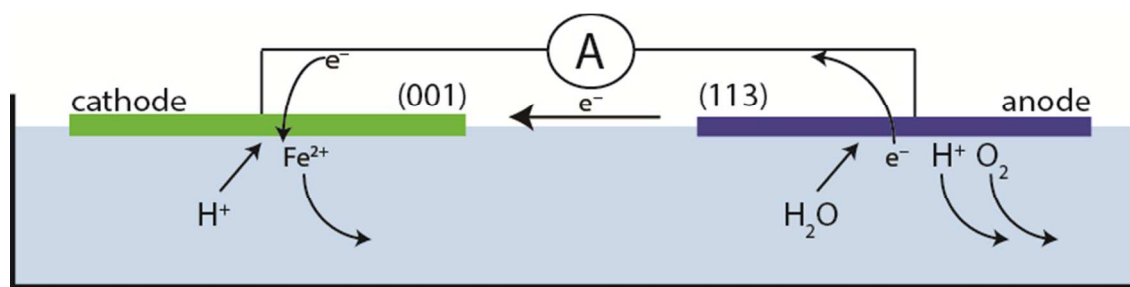
**Figure S1 Schematic diagram of electron transfer during ZRA experiments. Electrons are injected into the anode (eg (113)) through a water oxidation reaction and are ejected from the cathode (eg (001)) into the solution through a hematite dissolution reaction ($Fe^{3+}_{(s)} + e^- \rightarrow Fe^{2+}_{(aq)}$).**
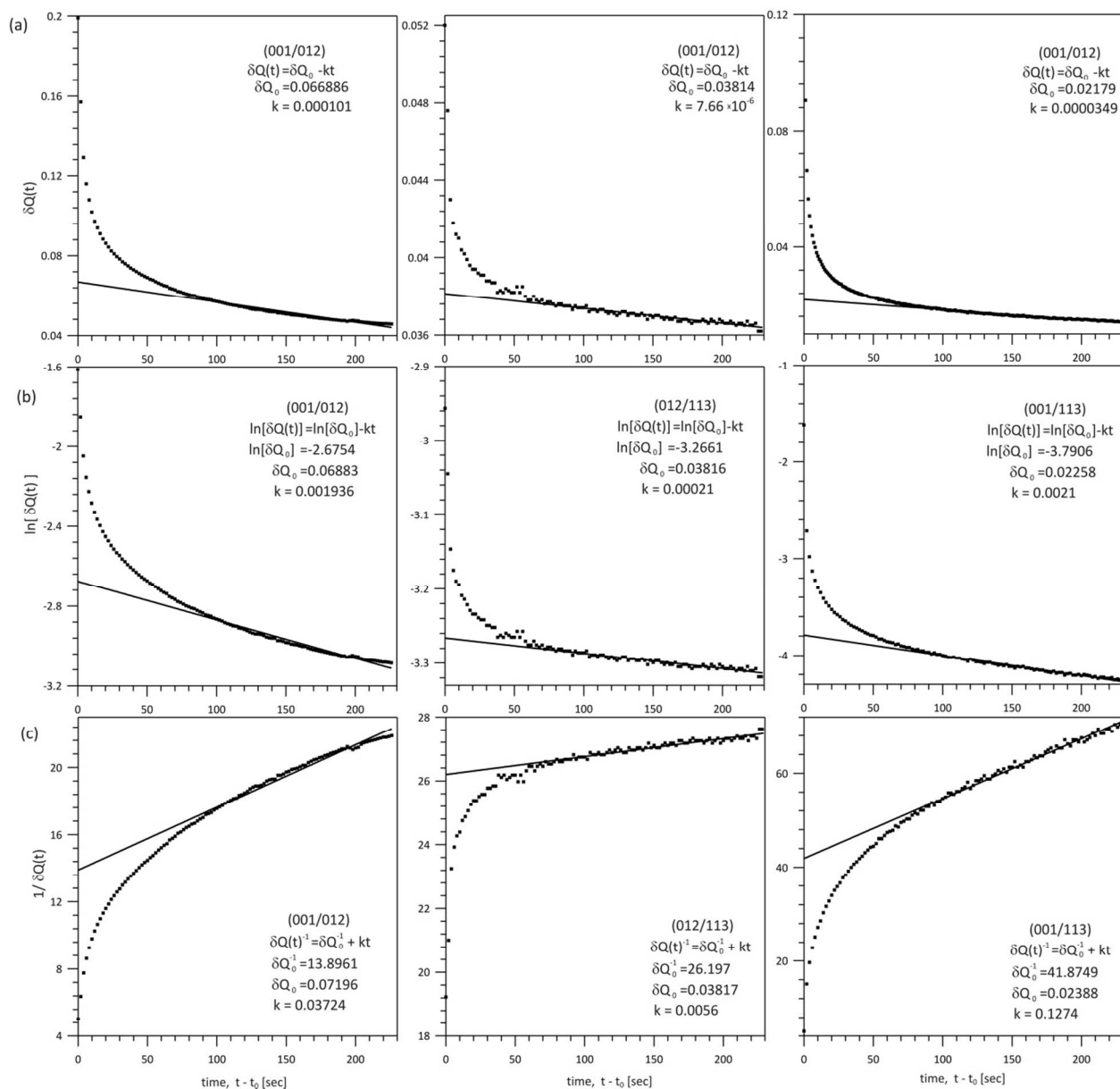
**Figure S2** Fitting the zero- (a), first (b) and second (c) order equations to the measured time-dependent currents (kinetics at the initial time cannot be described correctly by any of the equations above. We conclude that the charge flow is not determined by the zero ($\frac{d[e^-]}{dt} \sim const$), first ($\frac{d[e^-]}{dt} \sim k[e^-]$) or second ($\frac{d[e^-]}{dt} \sim k[e^-]^2$) order process.
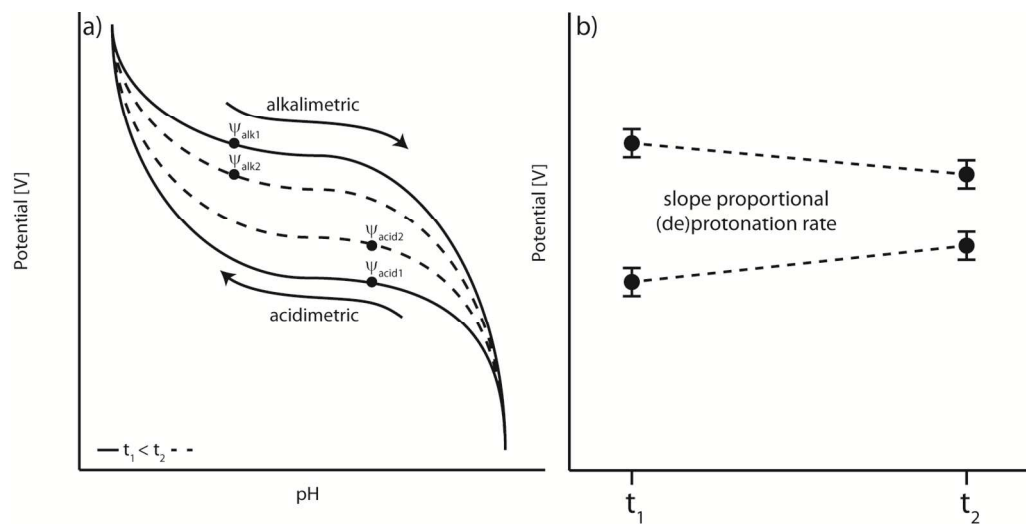
**Figure S3** Schematic diagram of the procedure used to approximate the protonation and deprotonation rate of hematite surfaces using hysteretic titrations. Hysteretic titration data, shown schematically here (a), was used to determine (de)protonation rates (b). The data used to calculate the data presented Figure 5 of the main manuscript was taken from data previously published by us. [1]

**References:**

1. Chatman, S.; Zarzycki, P.; Preočanin, T.; Rosso, K. M., Effect of Surface Site Interactions on Potentiometric Titration of Hematite ($\alpha$ $Fe_2O_3$) Crystal Faces. *J. Colloid. Interf. Sci.* **2013,** *391*, 125-134.