# **Electronic Supplementary Information (ESI)**

# From Millimetres to Metres: The Critical Role of Current Density Distributions in Photo-Electrochemical Reactor Design

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**Small scale electrode characterisation.** The power density with which  $0.01 \times 0.06 \text{ m}^2 \text{ Ti}|\text{Sn}^{IV}-\text{Fe}_2O_3$  electrodes were irradiated as a function of wavelength is shown in Figure 1S (a); the optical equipment used is shown in Figure 1S (b). Having conducted micro-kinetic measurements in the absence of a neutral density filter, the power density was substantially greater than the Solar AM 1.5 (ASTM G173-O3 Reference Spectra), which is the standard spectrum for such measurements. However, as we are not introducing a new photo-active electrode material, focusing on material performance or reporting IPCE values, the discrepancy is not of critical importance. All values presented in the manuscript have been normalised. Furthermore, as the thickness of the quartz aperture and body of the electrolyte attenuating the incoming light will vary between the experimental equipment used by different researchers, the irradiation of a photo-electrochemical reactor by Solar AM 1.5 was not of critical importance.



Figure 1S. (a) Irradiance spectrum of the 300 W Xe arc lamp measured at the photo-electrochemical reactor position and (b) the optical setup used for the characterisation of  $0.01 \times 0.06 \text{ m}^2 \text{ Ti} |\text{Sn}^{\text{IV}}-\text{Fe}_2\text{O}_3$  electrodes.

**Large scale electrode characterisation.** The power density with which  $0.1 \times 0.1 \text{ m}^2 \text{ Ti} |\text{Sn}^{IV}\text{-Fe}_2O_3$  electrodes were irradiated is shown in Figure 2S (a) as a function of wavelength; the optical equipment used is shown in Figure 2S (b).



Figure 2S. (a) Irradiance spectrum of the 550 W Xe arc lamp measured at the photo-electrochemical reactor position and (b) the optical equipment used for the characterisation of  $0.1 \times 0.1 \text{ m}^2 \text{ Ti} |\text{Sn}^{\text{IV}}\text{-Fe}_2\text{O}_3$  electrodes.

#### Photo-oxidation kinetics.

Current was recorded as a function of applied electrode potential at four  $0.01 \times 0.06 \text{ m}^2 \text{ Ti}|\text{Sn}^{IV}-\text{Fe}_2O_3$  photo-electrodes in 1 M NaOH in the dark and under illumination at a scan rate of 10 mV s<sup>-1</sup>. Photo-current density, computed by subtracting the current density measured in the dark from the current density measured under illumination, is presented in Figure 3S. The electrodes were fabricated in separate experiments and were consequently characterised on different dates. Therefore, the current densities are presented in normalised form in order to account for the variation in the power output of the lamp with time. The results demonstrate reproducible photo-kinetics.



Figure 3S. Normalized oxygen evolution photo-currents at four  $0.01 \times 0.06 \text{ m}^2 \text{ Ti}|\text{Sn}^{\text{IV}}\text{-Fe}_2O_3$  electrodes in 1 M NaOH solution, recorded at a potential scan rate 10 mV s<sup>-1</sup>.

### Photo-electrochemical impedance spectroscopy.

Photo-electrochemical impedance spectroscopy (PEIS) using the 300 W light source described above was used to determine electron-hole recombination efficiencies and interfacial capacitance as a function of applied electrode potential at four 0.01×0.06 m<sup>2</sup> electrodes. An equivalent electrical circuit, shown in Figure 5 (main manuscript), with two time constants was used to fit experimental data. Bode-phase plots and Nyquist plots are shown in Figure 4S, Figure 5S and Figure 6S.



Figure 4S. Bode-phase plots recorded for Ti $|Sn^{V}-Fe_2O_3|$  electrode in 1 M NaOH solution at applied electrode potentials in the range 0.17  $\leq U_{applied}$  (SHE) / V  $\leq 0.82$ 

![](_page_4_Figure_2.jpeg)

Figure 5S. Nyquist plots recorded for Ti | Sn<sup>IV</sup>-Fe<sub>2</sub>O<sub>3</sub> electrode in 1 M NaOH solution at applied electrode potentials in the range  $0.17 \le U_{applied}$  (SHE) / V  $\le 0.82$ 

![](_page_5_Figure_0.jpeg)

Figure 6S. Zoomed Nyquist plots recorded at applied electrode potentials in the range  $0.17 \le U_{applied}$  (SHE) / V  $\le 0.82$ 

**Mott-Schottky plots.** Mott-Schottky plots generated from interfacial capacitance values that were determined by fitting the equivalent circuit in Figure 5 (main manuscript) to impedance data collected in the applied potential range  $0.12 \le U_{applied}$  (SHE) / V  $\le 0.82$ . The flat band potential values determined at four electrodes are presented in Table 1S.

![](_page_5_Figure_3.jpeg)

Figure 7S. Mott-Schottky plots obtained for Ti|Sn<sup>IV</sup>-Fe<sub>2</sub>O<sub>3</sub> electrode in 1 M NaOH solution from interfacial capacitance values that were determined from PEIS data at applied electrode potentials in the range  $0.12 \le U_{applied}$  (SHE) / V  $\le 0.82$ 

Table 1S. Mott-Schottky plot gradients (linear sections indicated in Figure 7S) and flat band potential values determined on four  $Ti|Sn^{IV}-Fe_2O_3$  electrodes in 1 M NaOH solution.

Sample	dC <sup>-2</sup> <sub>SC</sub> / dU <sub>applied</sub>	<i>U</i> <sub>FB</sub> / V (SHE)	<i>U</i> <sub>FB</sub> / V (RHE)
1	10.6	0.11	0.91
2	16.7	0.18	0.99
3	17.0	0.16	0.96
4	14.7	0.21	1.01
Average		0.16 (± 0.022)	0.96 (± 0.022)

**Recombination kinetics.** The interfacial charge transfer efficiencies computed as a function of band bending at four different  $Ti|Sn^{IV}-Fe_2O_3$  electrodes in 1 M NaOH solution are shown in Figure 8S. Parameters A and B in Equation (1), obtained non-linear regression fitting, are presented in Table 2S.

![](_page_6_Figure_3.jpeg)

Figure 8S. Effect of band bending  $(U_{applied} - U_{FB})$  on interfacial charge transfer efficiencies,  $\Phi = f(\phi_{SC})$ , at Ti|Sn<sup>IV</sup>-Fe<sub>2</sub>O<sub>3</sub> electrodes. Dashed lines show the fits to the data obtained by non-linear regression.

Sample	A/1	B / V <sup>-1</sup>	
1	3.58(±0.189) × 10 <sup>-3</sup>	13.6(±0.333)	
2	9.67(±0.382) × 10 <sup>-4</sup>	14.7(±0.828)	
3	$3.31(\pm 0.755) \times 10^{-3}$	12.0(±0.476)	
4	$2.59(\pm 0.871) \times 10^{-3}$	13.0(±0.731)	
Average	$2.61(\pm 0.996) \times 10^{-3}$	13.3(±0.972)	

Table 2S. Parameters describing interfacial charge transfer efficiency

**Dielectric constant and charge carrier density.** In order to avoid an erroneous assumption about the value of  $\varepsilon_r$  for Ti|Sn<sup>IV</sup>-Fe<sub>2</sub>O<sub>3</sub> electrodes when computing  $n_0$  from the slopes of Mott-Schottky plots, we follow a calculation using which  $\varepsilon_r$  can be determined from experimental data.

The gradient of the Mott-Schottky plot is related to the dielectric constant by Equation (2):

$$\frac{d\left(C_{\rm sc}^{-2}\right)}{d\phi_{\rm sc}} = \frac{2}{\varepsilon_0 \varepsilon_{\rm r} e n_0} \tag{2}$$

The gradient of the plot of photo-current squared as a function of band bending is also dependent on the dielectric constant, as shown by one form of the Gärtner-Butler Equation (3):

$$\frac{d\left(j_{\text{photo}}^{2}\right)}{d\phi_{\text{SC}}} = \Phi \cdot (I_{0}\alpha)^{2} \frac{2\varepsilon_{0}\varepsilon_{\text{r}}e}{n_{0}}$$
(3)

Therefore, both gradients, which may be determined experimentally, could be used to compute  $\varepsilon_r$ , according to Equation (4):

$$\varepsilon_{\rm r} = \frac{1}{\Phi \varepsilon_{\rm o} e I_{\rm o} \alpha} \sqrt{\frac{d\left(j_{\rm photo}^2\right)}{d\phi_{\rm SC}}} / \frac{d\left(C_{\rm SC}^{-2}\right)}{d\phi_{\rm SC}}$$
(4)

 $\Phi$  has already been determined as a function of band bending. Hence,  $j_{\text{photo}}^2$  may be corrected by  $\Phi$  using equation (3). Spectrally resolved values of  $I \cdot \alpha$  can be expressed as  $\sum_{\lambda} (I_0 - I_x)_{\lambda} \cdot \alpha_{\lambda}$ , where

attenuation of photons by quartz and electrolyte is also taken into account. As the four Ti|Sn<sup>IV</sup>-Fe<sub>2</sub>O<sub>3</sub> electrodes were characterised on different dates, spectrally resolved values of  $l \cdot \alpha$  were adjusted for the calculation of  $\varepsilon_r$  for each electrode. The results, together with the computed charge carrier densities,  $n_0$ , are presented in Table 3S.

Table 3S. Dielectric constant and charge carrier density in hematite

Sample	$dj^2_{ m photo}$ / $d\phi_{ m SC}$ / $ m A^2~m^{-4}~V^{-1}$	$\sum ig(I_0 - I_xig)_{\!\lambda} \cdot lpha_{\lambda}$ / m <sup>-3</sup> s <sup>-1</sup>	ε	<i>n</i> <sub>0</sub> / m <sup>-3</sup>
1	908.7	1.71 × 10 <sup>29</sup>	38.3	3.48 × 10 <sup>27</sup>
2	804.1	1.25 × 10 <sup>29</sup>	39.0	2.13 × 10 <sup>27</sup>
4	640.5	1.25 × 10 <sup>29</sup>	37.4	2.57 × 10 <sup>27</sup>
Average			38.2(±0.463)	2.73(±0.398) × 10 <sup>27</sup>

**Temperature effects: Small-scale reactor** The change in electrolyte temperature was recorded over 4 hours in the 60 cm<sup>3</sup> reactor, during potentiostatic oxygen evolution at an  $0.01 \times 0.06$  m<sup>2</sup> Ti|Sn<sup>IV</sup>-Fe<sub>2</sub>O<sub>3</sub> anode at an applied potential of +0.7 V (SHE) (average measured current was 0.2 mA). The temperature was measured to rise by 0.17 C (relative to a reference 1M NaOH sample of the same volume). If this value is normalised by the electrolyte volume (60 cm<sup>3</sup>) and the total incident power (100 W), the rate of temperature increase is 8.27 C m<sup>-3</sup> W<sup>-1</sup> hr<sup>-1</sup>, which should have a negligible effect on electrode kinetics, measured typically in under four hours (including impedance measurements).

**Temperature effects: Large-scale reactor** Whilst temperature changes in the large reactor were limited during photo-anode characterisation by voltammetry (typically 10-15 minute duration), they were significant during the 24 hour tests performed at a constant applied cell bias. It was determined that 6 hours were required for the temperatures of both the anolyte and the catholyte to reach steady

state values of 42.5±2.5°C. Molar densities corresponding to this temperature range (25.69 – 26.11 dm<sup>3</sup> mol<sup>-1</sup>) were used for computing the faradaic H<sub>2</sub> evolution efficiencies,  $\mathcal{P}^{e}_{H2}$ , and also in the error analysis. We note that water vapour made negligible contribution to gas output measurements from either electrolyte as expected [i] and confirmed by experimental determination of gaseous output in the absence of applied bias (zero current).

**Scan rate influence** The influence of scan rate on the ratio between currents recorded at the planar  $0.1 \times 0.1$  m<sup>2</sup> photo-anode using electrode configurations depicted in Figure 1(a) and Figure 1(b) of the main manuscript is shown in Figure 9S.

![](_page_8_Figure_2.jpeg)

Figure 9S. Effect of potential scan rate on the ratio between currents recorded at the planar  $0.1 \times 0.1 \text{ m}^2$  photo-anode in 1 M NaOH solution using electrode configurations depicted in Figure 1(a) and Figure 1(b) of the main manuscript; the theoretical ratio based on the 56 % open area of the Ti|Pt mesh through which the photo-anode was illuminated in configuration (b) is also shown.

**Faradaic efficiency of H<sub>2</sub> evolution** The charge passed during 24 hour photo-assisted electrolysis at an applied cell bias of 1.6 V is shown in Figure 10S for the cases of planar and perforated photo-anodes in 0.1 M and 1 M NaOH solutions. The corresponding H<sub>2</sub> gas measurements are presented in Figure 11S.

<sup>[</sup>i] J. Balej, Int. J. Hydrogen Energy, 1985, 10, 233

![](_page_9_Figure_0.jpeg)

Figure 10S. Charge passed during photo-assisted electrolysis utilising planar and perforated  $0.1 \times 0.1 \text{ m}^2$  hematite photoelectrodes in 0.1 M and 1 M NaOH electrolytes.

![](_page_9_Figure_2.jpeg)

Figure 11S.  $H_2$  volume measured during photo-assisted electrolysis utilising planar and perforated  $0.1 \times 0.1 \text{ m}^2$  hematite photo-electrodes in 0.1 M and 1 M NaOH electrolytes.

## Modelling

The modelling was performed in COMSOL Multiphysics 4.4 with a Batteries and Fuel Cells module and LiveLink for MATLAB using an Intel<sup>®</sup> Core<sup>™</sup> i7-3770 CPU @ 3.40 GHz processor with a 16.0 GB RAM and 64-bit operating system.

**CPU and solution times** During the computation of results presented in Figure 11 and Figure 12 (main manuscript) the CPU utilisation was up to 58 % for the model with the planar anode and up to 63 % for the model with the perforated anode. The solution times for the planar and perforated anode models are shown below. These measurements were taken for a single condition at steady state; this means fixed material and geometrical properties and a single potential. Included are solution times for the cases of the linearized and non-linearized Butler-Volmer (B-V) equations describing cathodic kinetics.

<u>Planar anode - Fine mesh (number of degrees of freedom = 96,407)</u> Solution time = 10 seconds (linearized B-V) Solution time = 71 seconds (B-V)

Perforated anode - Fine mesh (number of degrees of freedom = 224,832) Solution time = 34 seconds (linearized B-V) Solution time = 224 seconds (B-V)

**Convergence study** We performed convergence studies at applied anode potentials of +0.3 V (SHE) and +0.7 V (SHE) in 1 M NaOH electrolyte in order to verify the suitability of the chosen tolerance of 0.001.

Anode potential: +0.3 V (SHE) Tolerance: 0.01 Solution time = 26 s; Dark current =  $1.62407 \times 10^{-5}$  A; Photo-current =  $2.61435 \times 10^{-4}$  A. Tolerance: 0.001 Solution time = 36 s; Dark current =  $1.62407 \times 10^{-5}$  A; Photo-current =  $2.61435 \times 10^{-4}$  A. Tolerance: 1 × 10<sup>-6</sup> Solution time = 36 s; Dark current =  $1.62407 \times 10^{-5}$  A; Photo-current =  $2.61435 \times 10^{-4}$  A. Tolerance:  $1 \times 10^{-12}$ Solution time = 42 s; Dark current =  $1.62407 \times 10^{-5}$  A; Photo-current =  $2.61435 \times 10^{-4}$  A. Anode potential: +0.7 V (SHE) Tolerance: 0.01 Solution time = 25 s; Dark current =  $5.19675 \times 10^{-4}$  A; Photo-current = 0.02397 A. Tolerance: 0.001 Solution time = 25 s; Dark current =  $5.19675 \times 10^{-4}$  A; Photo-current = 0.02397 A. Tolerance:  $1 \times 10^{-6}$ Solution time = 33 s; Dark current =  $5.19675 \times 10^{-4}$  A; Photo-current = 0.02397 A. Tolerance:  $1 \times 10^{-12}$ Solution time = 43 s; Dark current =  $5.19675 \times 10^{-4}$  A; Photo-current = 0.02397 A.

Mesh independence studies We performed two mesh independence studies: one at an applied anode potential of +0.3 V (SHE) and the other at +0.7 V (SHE). Both demonstrated the same solution was generated with 'Fine' mesh as with the 'Finer' and 'Extra fine' meshes.

Anode potential: +0.3 V (SHE)

Fine mesh (1,016,745 domain elements; 139,382 boundary elements; 26,903 edge elements; number of degrees of freedom solved for 224,832)

Solution time = 36 s; Dark current =  $1.62407 \times 10^{-5}$  A; Photo-current =  $2.61435 \times 10^{-4}$  A.

Finer mesh (1,962,285 domain elements; 236,503 boundary elements; 38,429 edge elements; number of degrees of freedom solved for 423,745) Solution time = 92 s; Dark current =  $1.62407 \times 10^{-5}$  A; Photo-current =  $2.61435 \times 10^{-4}$  A.

Extra fine mesh (5,602,513 domain elements; 538,510 boundary elements; 59,721 edge elements; number of degrees of freedom solved for 1,161,973) Solution time = 233 s; Dark current =  $1.62406 \times 10^{-5}$  A; Photo-current =  $2.61434 \times 10^{-4}$  A.

Anode potential: +0.7 V (SHE)

Fine mesh (1,016,745 domain elements; 139,382 boundary elements; 26,903 edge elements; number of degrees of freedom solved for 224,832).

Solution time = 34 s; Dark current =  $5.19675 \times 10^{-4}$  A; Photo-current = 0.02397 A.

Finer mesh (1,962,285 domain elements; 236,503 boundary elements; 38,429 edge elements; number of degrees of freedom solved for 423,745) Solution time = 71 s; Dark current =  $5.196 \times 10^{-4}$  A; Photo-current = 0.02397 A.

Extra fine mesh (5,602,513 domain elements; 538,510 boundary elements; 59,721 edge elements; number of degrees of freedom solved for 1,161,973)

Solution time = 245 s; Dark current =  $5.19479 \times 10^{-4}$  A; Photo-current = 0.02397 A.