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# Multiphysics model for assessing photoelectrochemical phenomena under concentrated irradiation

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# ABSTRACT

A multiphysics model was developed for a photoelectrochemical (PEC) cell at the device level to simulate water splitting operating under concentrated irradiation (between 50 to 600 kW m<sup>-2</sup>). The 2D model couples charge, heat, mass, photon, and momentum transfer to predict local current densities, potential distributions, temperature profiles, volumetric gas fractions, pressure, and velocities profiles in the electrolyte. Electrode kinetics and electrolyte resistance were considered for the electrochemical processes, and two-phase bubblyflow under laminar conditions for momentum transfer. The effects of bubbles on the incident photon flux and the thermal and electrical conductivities of the electrolyte were also considered. Photocurrent densities were estimated using a semiempirical correlations dependent on potential, charge transfer efficiencies, and temperature. The model was applied to a custom-made cell utilising a spray pyrolysed Sn-doped Fe<sub>2</sub>O<sub>3</sub> photoanode, a material with well-known photoelectrochemical behaviour and stability. Transparent conductive glass and titanium foil were investigated as two possible photoanode substrates. Predictions indicate that commercial conductive glasses are not suitable substrates due to a significant ohmic drop caused by high current densities. The model illustrates that thermal and bubble management are critical to improving the overall performance of a PEC cell subjected to high photon flux. Furthermore, the model can be used to decouple the phenomena that occur under such conditions and could assist in the study of photoelectrode materials under high irradiance.

#### 1. Introduction

Suitable photoelectrode materials are known to be the main bottleneck for the large-scale deployment of photoelectrochemical (PEC) devices for the production of solar fuels [1]. These semiconducting materials must be efficient, stable, and scalable, although usually only two out of three of these qualities are met simultaneously. For example, Fe<sub>2</sub>O<sub>3</sub> is an extensively researched photoelectrode material, known for its long-lasting properties and facile synthesis; however, the position of its band edges and high recombination rates, resulting in low efficiencies [2,3], preclude hematite from being used in real applications. Complex photoelectrodes with laborious synthesis, e.g. III-V tandem absorbers (GaInP, GaAs, GaP etc.) coupled with RuO<sub>x</sub> and PtRu catalysts [4], have not only been proven highly efficient for water splitting but also have been able to do it spontaneously, however with significant challenges of stability [4]. The strategy of using solar concentration to improve device power density and scalability has received greater attention [5]. Concentrated light would permit the use of smaller photoelectrodes reducing material needs and costs, and it

would facilitate the beneficial miniaturisation of PEC reactor components to an equivalent scale of electrolysis (based on power density). Furthermore, if devices are designed with proper thermal integration, overall efficiency can be improved due to increased reaction kinetics at the surface, lower overpotentials, lower thermodynamic requirements for water splitting [6] while making possible the co-generation of heat and fuel [7]. These advantages have been proposed to improve the economic potential of such systems [8,9]; however, challenges remain in the design and implementation of PEC devices that utilise solar concentration. Furthermore, the behaviour of semiconducting materials for PEC applications at high irradiance (>100 kW  $m^{-2}$ ) and high surface temperatures (> 50 °C) has been rarely explored; hence, charge transfer rates, flat band potentials, and carrier densities have been seldom reported in the literature under these conditions, which hinders the realisation of reliable models and devices for high photon flux applications.

Solar concentration has been implemented in a number of integrated PEC devices (e.g. PV + electrolyser or PV + PEC), when illuminated with concentrated light at 474 kW m<sup>-2</sup> [6], 9.33 kW m<sup>-2</sup>

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Nomenclature	
α	Charge transfer coefficient (–)
α,	Spectral absorptivity at $x (m^{-1})$
m.	Mass flux of species <i>i</i> (kg m <sup>-2</sup> s <sup>-1</sup> )
'n.	Molar flux of species <i>i</i> (mol m <sup>-2</sup> s <sup>-1</sup> )
n	Overpotential (V)
ч И	Dvnamic viscosity (Pa s)
<i>ь</i>	Volumetric fraction of gas (1)
τg Φι	Volumetric fraction of liquid (1)
$\Phi_{\rm hulle}$	Charge transfer efficiency in the bulk semi-
bulk	conductor (1)
$\Phi_{ m surface}$	Charge transfer efficiency at the surface (1)
ρ	Density (kg m <sup>-3</sup> )
σ	Electrical conductivity (S $m^{-1}$ )
$ au_{\lambda}$	Spectral transmittance (1)
v <sub>e</sub>	Electron stoichiometry (–)
$v_i$	Stoichiometry constant of species i (-)
$\varepsilon_0$	Vacuum permittivity, $8.854 \times 10^{-12}$ (F m <sup>-1</sup> )
ε <sub>r</sub>	Relative permittivity (–)
$\xi_T$	Coefficient for charge transfer vs. tempera-
	ture (–)
а	Specific superficial area (m <sup>2</sup> kg <sup>-1</sup> )
$A_a$	Anodic Tafel constant (V)
$A_i$	Cross sectional area for transfer of specie i
	(m <sup>2</sup> )
c <sub>i</sub>	Molar concentration of species $i \pmod{m^{-3}}$
$C_p$	Specific heat capacity (J $kg^{-1} K^{-1}$ )
$d_b$	Diameter of bubbles (m)
$D_i$	Diffusion coefficient of species $i$ (m s <sup>-2</sup> )
d <sub>i</sub>	Path length for specie <i>i</i> (m)
E	Potential (V)
e	Electronic charge, $1.6022 \times 10^{-19}$ (C)
E <sub>applied</sub>	Applied electrode potential (V)
Ecorrected	Electrode potential corrected by ohmic drop
F	(V) Elat hand notantial (V)
L <sub>fb</sub>	Fiat balle potential (V) Earders constant $06484.6$ (C mal <sup>-1</sup> )
Г а	Faraday constant, 90484.0 (C mor ) Gravity constant, 9.8 (m $s^{-2}$ )
8 1	Incident photon flux $(m^{-2} e^{-1})$
I I	Transmitted photon flux at $x (m^{-2} s^{-1})$
	Current (A)
i	Current density (A $m^{-2}$ )
j	Exchange current density (A $m^{-2}$ )
jo İcp	Current density according to Gartner-Butler
JGB	equation (A $m^{-2}$ )
İnh	Photocurrent density (A m <sup>-2</sup> )
k k	Thermal conductivity (W $m^{-1}$ K <sup>-1</sup> )
$K_{h}$	Bubble scattering constant (–)
1	Optical path length (m)
$M_i$	Molecular mass of species <i>i</i> (mol m <sup><math>-2</math></sup> s <sup><math>-1</math></sup> )
n <sub>o</sub>	Charge carrier concentration $(m^{-3})$
Р	Irradiance (W m <sup>-2</sup> )
р	Gauge pressure (Pa)
$P_{\lambda}$	Spectral irradiance (W m <sup>-2</sup> nm <sup>-1</sup> )
$P_{e,q,b}$	Irradiance transmitted through electrolyte,
· • ·	quartz window and bubbles (W $m^{-2}$ )
$P_{e,q}$	Irradiance transmitted through electrolyte
	and quartz window (W $m^{-2}$ )

0,	Generated heat (W $m^{-3}$ )
$\tilde{R}$	Ideal gas constant, 8.314 (J mol <sup><math>-1</math></sup> K <sup><math>-1</math></sup> )
$R_i$	Molar generation of species $i \pmod{m^{-3}}$
$R_s$	Unaccounted resistance ( $\Omega$ )
и	Velocity (m s <sup>-1</sup> )
Ζ.	Number of transferred electrons (-)
Т	Temperature (K)

[10], 207 kW m<sup>-2</sup> [11],  $C \simeq 250$  [12] and  $C \simeq 500$  [13] (where C is the geometric area concentration). A more comprehensive list of devices operating at concentrated irradiance can be found in the SolarFuel Database [14]. A few models have been developed for integrated PV + electrolyser devices operating up to 1000 suns [15,16] showing that flow rate control and thermal management are critical for synergetic integration. In addition to the constraints related to heat management, a 'pure' PEC cell (i.e. with one or more semiconductor-electrolyte junctions) operating under concentrated irradiation must be designed taking into account the increased ohmic drop in the photoelectrode and substrate; furthermore, unknown e-h transfer kinetics under these conditions and a higher degree of integration (c.f. PV + electrolyser) make it difficult to predict and assess the performance of individual components of the cell. For this, a PEC cell capable of testing photoelectrode materials under high photon fluxes and a model to decouple the effects of different phenomena is necessary. However, only a handful of studies have been reported on PEC cells operating under concentrated light, with irradiances typically below 30 kW  $m^{-2}$ .

An early example of a PEC cell under concentrated irradiation (1 - 10 kW  $\mbox{m}^{-2}\mbox{)}$  used p-type  $\mbox{GaInP}_2$  coupled to n-type hematite to spontaneously split water [17]. The influence of light intensity on the open circuit potential and the short circuit current density was reported. Whilst low efficiencies were obtained (ca. 0.0007%), it was shown that there is a non-linear relationship between light intensity and photocurrent; and that the open circuit potential improved for both photoelectrodes, *i.e.* decreased for the photoanode and increased for the photocathode. A decade earlier, Khasalev and Turner [18] managed to achieve an efficiency of 12.4% with a monolithic PV-PEC cell under ca. 11 kW m<sup>-2</sup>, although it was not reported how the device performed at different light intensities. More recently, Vilanova et al. [19] reported a scaled-up PEC cell (200 cm<sup>2</sup>) that splits water under moderately concentrated light (1 to 13 kW m<sup>-2</sup>) and uses a hematite photoanode. A non-linear relationship was also found between photocurrent densities and irradiance caused by the low electrical conductivity of the glass substrate; because of this, photoanodes were built modularly [20] with the aim of minimising the ohmic drop across the conductive glass substrate. However, the non-linear behaviour continued, and it was partially attributed to recombination phenomena in the semiconductor. On the contrary, Segev et al. have found a linear behaviour between photocurrent density and power density, after correcting for ohmic potential drop (34–36  $\Omega$ ), for hematite irradiated between 1 and 27 kW m<sup>-2</sup> [21]; these results were similar to those obtained by Le Formal et al. [22] in a narrower power density range (0.16–1.29 kW m<sup>-2</sup>) and Gupta et al. [23] for LaFeO3 photocathodes assessed between 1 and 18  $kW\ m^{-2}.$  As seen from the above studies, there is a clear absence of models and experimental studies of PEC materials operating under higher irradiances (> 30 kW m<sup>-2</sup>) and an understanding of the intrinsic material properties versus cell design on the performance. Hence, models to decouple thermal, bubble and ohmic drop effects on the performance of photoelectrodes are necessary to accurately analyse the experimental data obtained under the aforementioned conditions.

With concentrated irradiance, the temperature at the surface of the photoelectrode will increase, which could have conflicting effects on the performance, because of the temperature dependence of charge transfer efficiencies, kinetics, and thermodynamics. Although there is



**Fig. 1.** Schematic of the high-flux photoelectrochemical (HFPEC) setup at system level, not to scale. WE (FTO |  $Fe_2O_3$  or Ti |  $Fe_2O_3$ ), CE and RE stand for Working Electrode, Counter Electrode, and Reference Electrode, respectively.

compelling evidence [24–26] suggesting that surface and bulk electronhole recombination rates are strongly affected by temperature, this effect has rarely been studied. Carrier density and movement have been found to increase with temperature for  $CuWO_4$  photoelectrodes, but these improvements can be offset by increased recombination rates at temperatures higher than 70 °C [27]. A more resolved mechanism of photocurrent-temperature dependence has recently been proposed for hematite photoanodes [28]; several 'temperature coefficients' were used to describe the relationship between photovoltage, photocurrent, and dark current with temperature. It was found that the reaction kinetics at the surface, being the limiting step during charge transfer, plays a critical role in the temperature-dependence phenomenon.

Here, we present a multiphysics model and preliminary experimental validation of a novel PEC cell operating under concentrated irradiation (50 - 600 kW m<sup>-2</sup>) outlined in Fig. 1. This cell was designed to test and analyse PEC materials under controlled temperature and high flux conditions. Hematite was used as a case study due to its wellknown and predictable PEC behaviour [29]. We studied the effects of substrate material [30], electrolyte flow [31], bubbles [32], current densities distribution [33,34], and photoelectrode temperature [24] on the performance of a PEC cell and PEC materials subjected to high photon fluxes. The model accounts for five coupled physics: heat, mass, momentum, photon, and charge transfer. Conductive glass substrates were found to be the main contributor to ohmic potential losses, followed by ohmic drop in the electrolyte. A semiempirical model was implemented to incorporate the dependence of charge transfer efficiencies with temperature. Here, we report for the first time data of PEC cells and materials exposed to irradiances greater than 30 kW m<sup>-2</sup>, which are described by an accurate multiphysics model. This work offers one of the first investigations of the deconvolution of different aspects that contribute to the losses observed in PEC devices when performing under concentrated irradiation and allows for the deconvolution and analysis of transport processes in PEC materials.

#### 2. Theoretical treatment

#### 2.1. Heat and mass transfer

Heat and mass transfer processes were modelled using the standard steady-state energy and mass balance equations (Eqs. (1) and (2)). As the semiconductor layer is assumed to be extremely thin compared to the dimensions of all other materials, it was neglected from the thermal simulation (i.e. the composite photoelectrode thermal properties can be accurately modelled using the thermal properties of the substrate). Furthermore, only the electrolyte domain was considered for the mass transfer model. No mass or heat generation were assumed in the interior domain of the simulated materials (stainless steel body, electrolyte, photoelectrode, gasket). Heat generation from absorbed high flux light was applied to the illuminated photoelectrode | electrolyte boundary, and mass generation was applied to the electrochemical boundaries. Convection and conduction were considered in the incompressible fluid for heat transfer, whereas only thermal conduction was modelled for solids. The concentration of hydroxide ions was modelled as an aqueous dilute domain with mass transfer via diffusion and convection.

$$\rho C_p u \cdot \nabla T - \nabla \cdot k \nabla T = 0 \tag{1}$$

$$u \cdot \nabla c_i - \nabla \cdot D_i \nabla c_i = 0 \tag{2}$$

#### 2.2. Momentum transfer and bubbly-flow

A steady-state, laminar, Euler–Euler model was used for the twophase fluid flow, *i.e.* gas bubbles and liquid, with the following assumptions: (*i*) the density of the gas is much smaller than that of the liquid, (*ii*) the two phases are subjected to the same pressure field, (*iii*) the velocity of the bubbles is determined by viscous and pressure forces, and (*iv*) the gas bubbles are spherical and 50  $\mu$ m in diameter [32,35,36]. Consequently, the momentum transfer equation can be simplified to:

$$\phi_l \rho_l u_l \cdot \nabla u_l = -\nabla p + \nabla \cdot \left[ \phi_l \mu_l \left( \nabla u_l - \frac{2}{3} (\nabla \cdot u_l) I \right) \right] + \phi_l \rho_l g \tag{3}$$

with the corresponding continuity equations for liquid and gas as follows:

$$\nabla \cdot (\phi_l \rho_l u_l + \phi_g \rho_g u_g) = 0 \tag{4}$$

$$\nabla \cdot (\phi_{\sigma} \rho_{\sigma} u_{\sigma}) = 0 \tag{5}$$

For the volumetric flows evaluated in this study  $(0.1 - 5 \text{ cm}^3 \text{ s}^{-1})$ , the Reynolds numbers were estimated to be between 500 and 2300 for the inlets and between 100 and 600 near the photoelectrode surface; hence, laminar flow can be assumed.

#### 2.3. Light attenuation and bubble scattering

Light attenuation was considered through a quartz window and liquid electrolyte. For this, the total transmittance spectrum (220–1000 nm) was determined for a quartz window (2 mm thick) and 1 M NaOH electrolyte with an optical path of 10.2 mm. Assuming a normal incidence of the light, the spectral irradiance on the surface of the sample,  $P_{q,e}$ , can be calculated from the transmittance of the quartz window, the transmittance of the electrolyte and the incident light irradiance as follows:

$$P_{(e,q),\lambda} = P_{\circ,\lambda} \times \tau_{quartz,\lambda} \times \tau_{electrolyte,\lambda}$$
(6)

In the case of bubble scattering, we assume a Poisson distribution for the number of bubbles in the path of rectilinear light rays and assume that zero bubbles must block light to pass through. Then, the fraction of light transmitted can be estimated as  $\exp(-K_bal/4)$  [37], where  $K_b$  is the total scattering coefficient, typically between 0.6 and 1.0 for oxygen evolving electrodes [32], l is the length of the optical path, and a the interfacial area per unit volume. Bhanawat and Pilon, who developed a detailed ray-tracing model of light transfer through bubbles, showed that there is a spectral dependence on the bubble-induced optical losses [38] and therefore  $K_b$  should be a function of wavelength. However, this effect is neglected in this work in order to reduce model complexity and is justified as the spectral optical losses do not change significantly below 800 nm.

Taking into account the following assumptions: (*i*) each bubble scatters a fixed amount of light, (*ii*) multiple scattering is not considered, (*iii*) bubbles are uniformly distributed in the volume, (*iv*) the light scattered from the effective bubble area is not absorbed by the photoelectrode, and (*v*) bubbles are perfectly spherical, the transmitted light through the bubbles can be calculated as:

$$P_{e,q,b} = P_{e,q} \exp\left(-\frac{K_b a l}{4}\right) = P_{e,q} \exp\left(-\frac{3K_b \phi_{g,\text{light}} l}{2d_b}\right)$$
(7)

Where  $P_{e,q,b}$  is the incident light on the sample corrected for scattering due to bubbles and attenuation by the quartz window and electrolyte.  $\phi_{g,\text{light}}$  is the average volumetric gas fraction in the illuminated volume and  $d_b$  is the average diameter of the bubbles. For this study,  $d_b = 50 \text{ }\mu\text{m}$  and  $K_b = 0.8$  were assumed, values that are in good agreement with experimentally measured bubble diameters [32,35,36] and total scattering coefficients [32].

In the case of a semitransparent substrate, *e.g.* FTO, the light that is not absorbed by the photoelectrode (substrate and hematite film) does not contribute to the generation of heat or charge on the surface of the photoelectrode. Consequently, the total power absorbed by the photoelectrode is estimated to be 25% of the incident light (see the Supporting Information in Fig. S3(b)) which is assumed to be thermally dissipated as heat. Only a minor fraction contributes to the electrical charge, which was assumed to be negligible in the heat balance. In the case of an opaque substrate, *e.g.* Ti foil, it can be assumed that all incident power contributes to heating.

#### 2.4. Electrochemical processes

Steady-state charge transfer *via* electrochemical reactions was modelled by assuming electroneutrality and negligible concentration gradients of hydroxide ions. The ionic current in the electrolyte can be estimated by using Faraday's law of electrolysis with the Nernst–Planck equation:

$$j_{ionic} = -F^2 \sum_i z_i^2 u_i c_i \nabla \phi_l \tag{8}$$

And then solving for the potential across the cell:

$$\Delta E = E_{O_2|H_2O} - E_{H_2O|H_2} + \eta_a + |\eta_c| + \sum_i \frac{Jd_i}{\sigma_i A_i}$$
(9)

At the cathode, dark currents were modelled using the Butler– Volmer equation for hydrogen evolution.

$$j_{c,dark} = j_{c,\circ} \left[ \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right]$$
(10)

At the anode, dark anodic currents were modelled assuming a Tafel behaviour. Hematite electrodes require relatively large overpotentials (> 100 mV) for oxygen evolution; hence, the reverse reaction can be neglected:

$$j_{a,dark} = j_{a,\circ} 10^{\eta/A_a} \tag{11}$$

Gas-evolving surfaces were coupled to two-phase bubbly-flow and diluted species physics *via* Faraday's law of electrolysis. A faradaic efficiency of 100% was assumed and stoichiometry coefficients were used according to the splitting of water in an alkaline environment, Eqs. (12) and (13).

$$2H_2O + 2e^- \Leftrightarrow H_2 + 2OH^- E_{H_2O|H_2} = 0 V vs. RHE$$
 (12)

$$O_2 + 2H_2O + 4e^- \Leftrightarrow 4OH^- E_{O_2|H_2O} = 1.23 \text{ V } vs. \text{ RHE}$$
 (13)

## 2.5. Photocurrent density predictions

Photocurrent densities were estimated using a semiempirical relationship outlined in previous work [29,34]. The updated version of this relationship now includes a temperature-dependent term that accounts for improved charge transfer in the semiconductor at higher temperatures. Estimating photocurrents from first principles and properties of semiconducting materials is a challenging task. Suitable models have already been proposed: Piekner et al. developed a model to calculate the charge carrier collection of hematite photoanodes [39], Gaudy et al. developed a similar model to estimate photogenerated currents in lanthanum titanium oxynitride photoanodes [40], and Huang et al. developed a series of temperature-dependent coefficients to elucidate the mechanism of charge transfer at higher temperatures [28]. However, these models require complex techniques and carefully measured properties for each material, which in our case were not available; hence, we resorted to using a semiempirical model based on easily measurable data, e.g. voltammograms, chronoamperometry, and electrochemical impedance spectroscopy spectra in absence and presence of illumination

In our model, the photocurrent density was predicted using a semiempirical model where the Gartner-Butler equation [41,42] was modified by the charge transfer efficiencies associated with additional recombination processes in the bulk ( $\Phi_{\text{bulk}}$ ) and surface ( $\Phi_{\text{surface}}$ ) [43], which are not accounted for in the ideal Gartner-Butler relationship, but that can be determined experimentally.

$$j_{GB} = \left(\frac{2e\left(\sum_{\lambda} (I_{o} - I_{x})_{\lambda} \alpha_{\lambda}\right)^{2} \epsilon_{0} \epsilon_{r}}{n_{o}}\right)^{1/2} \times (E_{\text{applied}} - E_{fb})^{1/2}$$
(14)

$$j_{ph} = j_{GB} \times \Phi_{\text{surface}} \times \Phi_{\text{bulk}} \tag{15}$$

The surface ( $\Phi_{surface}$ ) and bulk ( $\Phi_{bulk}$ ) charge transfer efficiencies can be experimentally estimated by assessing photoelectrodes under simulated solar light (*ca.* 1 kW m<sup>-2</sup>) at room temperature.  $\Phi_{surface}$  can be measured *via* electrochemical impedance spectroscopy or chopped light chronoamperometry [44,45], and then fitted to a logistic function in terms of the applied electrode potential:

$$\Phi_{\text{surface}} = \frac{A}{1 + \exp\left(-B(E_{\text{applied}} - C)\right)}$$
(16)

where A, B and C are fitted constants and are characteristic of a given photoelectrode material. For a logistic function, it holds that  $A = \Phi_{\text{surface,max}} \approx 1$ , *B* is the logistic growth rate, and  $C = E_{\text{mid value}}$  when  $\Phi_{\text{surface}} \approx 0.5$ .

In the case of  $\Phi_{\rm hulk}$ , it can be experimentally determined by calculating the ratio between  $J_{GB}$  and the photocurrent obtained in the absence of surface recombination, e.g. in the presence of a hole scavenger. Although, some semiconductors might exhibit current doubling effects when using hole scavengers, it has been confirmed that using  $H_2O_2$ as hole scavenger does not incur in current doubling for hematite photoelectrodes [29,43,46].  $\Phi_{\text{bulk}}$  is relatively constant with the potential for Sn-doped Fe<sub>2</sub>O<sub>3</sub> [29]. In addition, it is possible to include a temperature-dependent variable that accounts for increased charge transfer at higher temperatures near the photoelectrode surface. This effect has been experimentally observed in metal oxide photoelectrodes in the presence [24] and absence [25] of hole scavengers at temperatures between 25 and 65 °C. Therefore, we formulate an empirical linear relationship from the data extracted from Ref. [24], where the charge transfer efficiency in the bulk at 25 °C is multiplied by a correction factor as a function of temperature. For this,  $\Phi_{\rm bulk}$  is first expressed as a function of temperature:

$$\boldsymbol{\Phi}_{\text{bulk},T} = \begin{bmatrix} j_{ph,T} \\ j_{GB} \end{bmatrix}_{\boldsymbol{\Phi}_{\text{surface}}=1}$$
(17)

where  $[j_{ph,T}]_{\varPhi_{\text{surface}}=1}$  is the photocurrent density experimentally measured at different temperatures in the presence of a hole scavenger

#### Table 1

Effective properties used in the model for different physics.

Rheological	Thermal	Electrochemical
$\mu_{eff} = \mu_l$ $\rho_{eff} = \phi_l \rho_l + \phi_g \rho_g$	$ \begin{aligned} k_{eff} &= \phi_l k_l \\ C_{p,eff} &= \phi_l C_{p,l} + \phi_g C_{p,g} \end{aligned} $	$\begin{split} \sigma_{eff} &= (1-\phi_g)^{1.5} \sigma_l \\ j_{\circ,eff} &= (1-\phi_g) j_\circ \end{split}$

or estimated by dividing the photocurrent density by  $\Phi_{\text{surface}}$ . Taking  $\Phi_{\text{bulk}(25 \,^{\circ}\text{C})}$  as a reference, we find the following fitted linear relationship (see Fig. S7(a) in the Supporting Information):

$$\boldsymbol{\Phi}_{\text{bulk},T} = \boldsymbol{\Phi}_{\text{bulk}(25\,^{\circ}\text{C})} \times \boldsymbol{\xi}_{T}(T - 25\,^{\circ}\text{C}) \tag{18}$$

where *T* is the temperature on the surface of the photoelectrode and  $\xi_T$  is a coefficient that can be determined from voltammograms at different temperatures.  $\xi_T$  was found to be relatively constant for hematite between 1.0 and 1.7 V vs. RHE and can be calculated as follows:

$$\xi_T = \left[ \frac{\partial \left( j_{ph,T} / j_{ph,25 \, \circ \, \mathrm{C}} \right)}{\partial T} \right]_{\boldsymbol{\Phi}_{\mathrm{surface}} = 1}$$
(19)

Then, we can express the photocurrent density as:

$$j_{ph} = j_{GB} \times \Phi_{\text{surface}} \times \Phi_{\text{bulk}(25 \,^{\circ}\text{C})} \times \xi_T (T - 25 \,^{\circ}\text{C})$$
(20)

where  $j_{GB}$  and  $\Phi_{\text{surface}}$  are functions of electrode potential and material properties, while  $\Phi_{\text{bulk}(25 \circ \text{C})}$  and  $\xi_T$  are measurable constants for a given material. More details about these calculations and the linear regressions used to estimate  $\xi_T$  can be found in the Supporting Information in section S6.

#### 2.6. Effective and temperature dependant properties

To decrease the complexity of the model, some temperaturedependent two-phase flow parameters are replaced by their effective counterparts, which are summarised in Table 1. This is justified as the changes fluid temperature are relatively small, gas fractions are relatively small, and the Euler–Euler bubbly-flow model already assumes averaged properties in the fluid domain; this is because in that model the individual trajectories of bubbles are not traced. For the rheological and thermal properties, the effective parameters were calculated on the basis of volumetric average. Effective electrical conductivities were determined using a Bruggeman relationship in terms of the gas volume fraction in the electrolyte. The electrochemically active area was also a function of the local gas volume fraction at the interface, and it was assumed that bubble coverage renders the surface electrochemically inactive. These effective properties were replaced in Eqs. (1), (3), (9), (10) and (11).

For the properties that were considered temperature-dependent in this work (*i.e.* thermal and electrical conductivities, viscosities, densities, and specific heat capacities), the temperature was locally resolved *via* the heat transfer model. On the other hand, the following properties and parameters were assumed to be constant with temperature: equilibrium potential for oxygen and hydrogen evolution reactions, exchange current densities, tafel slopes, and surface charge transfer efficiencies and flat band potentials. The last four parameters are highly dependent on the properties of the photoelectrode, and can be widely different for the same material produced by different methods [47,48]; hence, a more detailed experimental study of the effect of temperature on these properties is necessary to fully account for these temperature-dependent effects.

#### 2.7. Limitations of the model

Whilst the model introduced in this work is both detailed and comprehensive, there are a number of model limitations that need to be highlighted: some of the electrochemical properties were not a function of temperature and OH<sup>-</sup> concentration, including exchange current

densities, equilibrium potentials, and surface charge transfer efficiencies. There is no desorption or absorption of gas in the electrolyte, and only two dimensions were considered. A more detailed description and justification for each of these limitations can be found in section S7 of the Supporting Information.

#### 3. Methods and materials

#### 3.1. High flux photoelectrochemcial (HFPEC) cell

A commercial solver (COMSOL Multiphysics 6.0) was used to solve the governing equations in a 2D projection of a custom-made high flux photoelectrochemical (HFPEC) cell. The HFPEC cell consisted of a body of stainless steel 316, two silicone gaskets 3 mm thick, a quartz window 2 mm thick, an EPDM o-ring, and an aluminium retainer for the quartz window. All tubing was made of polytetrafluoroethylene (PTFE). The beam of light was 5 mm in diameter and was directed toward the centre of the photoelectrode. Two substrates were evaluated: semitransparent FTO glass (Solaronix TC22-15, 2 mm) and titanium foil (99.7% Sigma Aldrich, 0.126 mm). The novel design of the HFPEC cell allowed the electrolyte to recirculate at the back of the substrate to prevent undesirable high temperatures. A Luggin capillary was implemented so that the reference electrode could be modelled as a point only a few millimetres away from the photoanode surface. The flow of the HFPEC was controlled by a peristaltic pump with an integrated pulsation dampener (KNF, FP70 KPDCB-4B), which can deliver volumetric flows between 0.5 and 10 cm<sup>3</sup> s<sup>-1</sup> at a maximum pressure of 200 kPa. A preliminary thermal study was necessary to select suitable operating conditions, so that the substrate and cell remained at low temperatures while preserving a laminar regime across the electrolyte.

High irradiances were modelled according to the specifications of the EPFL High Flux Solar Simulator (HFSS) [49]. The spectra of the Xe lamp can be found in the Supporting Information in Fig. S1. A single HFSS lamp can achieve light concentrations on the HFPEC between 30 and 700 kW m<sup>-2</sup>.

#### 3.2. Sn-doped hematite photoanodes

The photoanodes used for this inauguration study were Sn-doped  $Fe_2O_3$  films. Physical samples were fabricated by spray pyrolysis following a procedure previously reported [29]. Briefly, 0.1 M FeCl<sub>3</sub>.6H<sub>2</sub>O (>99%, Acros Organics) and 0.6 mM SnCl<sub>4</sub> (anhydrous, 99%, Thermo Fisher Scientific) were dissolved in absolute ethanol (99.8% Fisher Chemical). Sn<sup>4+</sup> concentration corresponded to *ca.* 1.3% doping by mass. The precursor was nebulised with a quartz spray nozzle (Meinhard, USA) at a height of 150 mm above the surface of the substrate, which was kept at 450 °C. 20 passes and 40 passes of precursor flowing at 2 cm<sup>3</sup>s<sup>-1</sup> were sprayed onto FTO and titanium foil, respectively. A 60 s rest between passes was necessary to allow the precursor to evaporate completely. The samples were then annealed at 400 °C for 1 h in air.

The photoelectrochemical properties of the samples were measured by voltammetry, chronoamperometry, and electrochemical impedance spectroscopy following protocols reported elsewhere [45,50,51]. The samples were evaluated in a three-electrode cell with an exposed/illuminated area of 8 mm in diameter on the working electrode, a Pt wire as the counter electrode and an RHE electrode (HydroFlex, Gaskatel) as the reference electrode. The cell used for this characterisation can be found in the Supporting Information in Fig. S4. All experiments were performed in 1 M NaOH aqueous solution. The samples were evaluated under 1 sun (*ca.* 1 kW m<sup>-2</sup>) using a LED light source (Versol-2, Newport), their spectra were measured with a spectrometer (Flame-S-XR1 with cosine corrector CC-3-UV-S, Ocean Insight) and the results can be found in Fig. S1 in the Supporting Information. The absorbance spectra of the samples can also be found in Fig. S2 and were measured using a UV–Vis spectrometer (UV-2600



Fig. 2. (a) Representation of the PEC cell, dashed lines indicating electrochemically active surfaces and red dot the illuminated area. (b) 1D representation of boundaries and properties used in the model for the different domains. (c) Sankey diagram of the typical light propagation through the modelled system for the  $FTO|Fe_2O_3$  sample. For the opaque  $Ti|Fe_2O_3$  sample no light can be transmitted and a larger fraction is absorbed.

Shimadzu) with an integrating sphere (ISR-2600PLUS Shimadzu). Interfacial charge transfer efficiencies ( $\Phi_{surface}$ ) were estimated by chopped light chronoamperometries (Fig. S5), while bulk charge transfer efficiencies ( $\Phi_{bulk}$ ) were estimated by dividing the photocurrent in the absence of superficial charge recombination by the theoretical limit imposed by the Gartner-Butler relationship, as described previously by Eq. (17) and as reported in Fig. S6(a,b,c) in the Supporting Information. The flat band potential and donor concentration were estimated using electrochemical impedance spectroscopy and the Mott-Schottky relationship [51], see Fig. S6(d) in the Supporting Information.

To estimate  $\Phi_{\text{bulk}}$  at different temperatures, voltammograms performed in the presence of glycerol, between 25 and 75 °C, were taken from Alhersh's work [24], these data and analysis can be found in the Supporting Information in Fig. S7.

# 3.3. Boundary conditions of computational model

A summary of the boundary conditions and domain properties can be found in Fig. 2(a,b). Light propagation and its approximate losses through the PEC cell can been seen in the Sankey diagram in Fig. 2(c). In the case of FTO substrates, ca. 25% of the light is absorbed by the photoelectrode, with the rest of light being transmitted or reflected. For opaque Ti substrates, ca. 80% of light is absorbed, with ca. 20% being reflected.

#### 3.3.1. Momentum transfer

To decrease the numerical complexity without impacting accuracy, a bubbly-flow model for the electrolyte flowing on top of the photoanode was used, whereas for the recirculated electrolyte on the back of the HFPEC cell only a liquid-flow was modelled. This simplification is justified because the average concentration of gas in the recirculated electrolyte after homogenisation is low enough ( $\phi_g < 0.001$ ) to not significantly affect the rheological and thermal properties of the flow in the back of the cell.

The inlet boundaries of the HFPEC (main inlet and recirculation inlet in the back) were modelled as fully developed flow; an average velocity was estimated for a given volumetric flow divided by the crosssectional area of the inlet. The volume fraction of the gas was assumed to be zero in both cases. The average pressure at the first outlet was assumed to be equal to the average pressure at the second inlet, and the second outlet was assumed to be open to the atmosphere.

The gas fluxes were imposed on the cathode and the anode surfaces, and they were equal to the mass flux originating from the hydrogen and oxygen evolution reactions, respectively. The mass fluxes were calculated using Faraday's law with a Faradaic efficiency of 100%. No slip condition, no wall movement, and no gas flux were assumed for the remaining walls in contact with the electrolyte.

#### 3.3.2. Mass transfer

In the same way as in bubbly-flow physics and with the aim of decreasing the complexity of the model, the concentration of hydroxide ions was only modelled for the electrolyte flowing on the photoanode. The recirculated electrolyte at the back of the cell was assumed to have a constant concentration. Therefore, the inlet of the HFPEC was set to  $c_{\rm OH^-} = 1000 \text{ mol m}^{-3}$ , while the mass fluxes at the cathode and photoanode surfaces were linked to the electrochemical reaction *via* Faraday's law.

#### 3.3.3. Heat transfer

All the exterior walls of the HFPEC cell were assumed as perfectly insulated. This assumption was experimentally confirmed by measuring the surface temperature of the exterior cell, which was found to be close to room temperature even during high-flux experiments. Furthermore, the results of the model confirm that the exterior temperatures are constant (*ca.* 20 °C) due to the fact that the heat flux is transferred almost exclusively from the substrate to the electrolyte, which in turn flows outside of the cell.

The first inlet of the cell was set at 20 °C, while the average temperature of the second inlet was assumed to be the average temperature of the first outlet. The light beam impacts the surface of the photoanode after being attenuated by the quartz window and electrolyte; hence, a boundary heat source is applied to the surface of the photoanode, which is assumed to be equal to the beam size (5 mm in diameter). From the measured absorbance spectra, it was estimated that only 25.52% of the irradiance is absorbed by the photoanode produced with semitransparent FTO (Fig. S3 in the Supporting Information); therefore, only a quarter of the applied irradiance is effectively converted to heat at the surface. Based on the same methodology, the photoelectrodes with a titanium foil substrate were estimated to absorb 79.3% of the irradiance and converted to heat. The previous assumptions do not take into account the amount of power converted to charge by the semiconductor; however, for the hematite films used in this study, the amount of power converted to charge is only a fraction (< 1%) and it can be assumed that it has negligible effects on heat transfer.

# 3.3.4. Charge transfer and electrochemical boundaries

A three-electrode setup was used and modelled. The top stainless steel part of the cell (cathode) served as a counter electrode, and the illuminated area at the photoanode surface acted as a working electrode. The RHE reference electrode was modelled as a point located near the photoanode surface; this point was located at the same position as the end point of the Luggin capillary placed in the real HFPEC cell. 1 M NaOH electrolyte was used to ensure the absence of mass transport limitations and to prevent any possible degradation of hematite photoanodes at high surface temperatures and photon fluxes. The photoelectrodes were coated with acrylic paint to limit the electrochemically active area to the size of the illuminated area.

An electrical ground was assumed for the exterior surface of the counter electrode. An electrode potential (*vs.* RHE) was applied to the external part of the photoanode near the reactor body. The position of this boundary was of significant importance for low-conducting substrates because of the severe effects caused by large ohmic drops.

The cathode surface was modelled as a platinised surface with current densities following the Butler–Volmer equation for hydrogen evolution reaction (HER). Because the cathode acts as a counter electrode, the catalytic properties for HER do not significantly impact the results of the model, as long as the area is large enough and does not kinetically limit the charge transfer through the cell, *i.e.* it has better kinetics than the oxygen evolving electrode. The photoanode surface had two electrochemical reactions applied: (*i*) dark current following a Tafel behaviour, and (*ii*) photocurrent densities following a modified Gartner-Butler relationship, as described in the theoretical section. These current densities were linked to mass transport and bubbly-flow physics to estimate the mass fluxes of hydroxide ions and evolved gas, respectively.

## 4. Results and discussion

#### 4.1. Thermal study

First, a simplified model was formulated to study the temperature and velocity profiles across the device for two different substrates (2 mm FTO and 0.13 mm Ti) when subjected to different concentrated irradiance (10 to 1000 kW m<sup>-2</sup>) and electrolyte flows (0.1 to 5 cm<sup>3</sup> s<sup>-1</sup>).

For this preliminary study, the only active physics were momentum and heat transfer. Bubble generation was not considered at this point to facilitate the convergence of the model at different flow rates. The results of this preliminary model were used to narrow down the conditions under which the HFPEC cell could operate safely; that is, minimising local temperatures and pressure losses, while maintaining laminar flow throughout the cell.

As Fig. 3 suggests, during all evaluated conditions, FTO can maintain the cell temperature below 100 °C, while Ti exceeded this temperature when using flow rates below 2 cm<sup>3</sup> s<sup>-1</sup>. The velocity profiles, as shown in Fig. S8(b), indicate that high local velocities are reached on both sides of the photoanode. This is highly beneficial for the performance of PEC cells under high irradiation as it improves the cooling effect, mass transport, and bubble removal as a result of the convective effect. The pressure drop across the cell was found to be directly proportional to the flow rate and never exceeds the limits of the peristaltic pump (< 200 kPa), even at the maximum flow rate assessed in the model (5 cm<sup>3</sup> s<sup>-1</sup>) as seen in Fig. S8(a) in the Supporting Information.

Taking these results into account, an optimal flow rate of  $3.5 \text{ cm}^3 \text{ s}^{-1}$  was selected to keep the maximum temperatures below 100 °C, even when the cell is subjected to an irradiance of 1000 kW m<sup>-2</sup>. Therefore, experimental studies and further parametric studies of the model were performed using this flow rate.

#### 4.2. Full model study

Fig. 4(a) and 4(c) show the photocurrent densities as a function of the potential under different irradiances for FTO and Ti substrates, respectively. The resistive contribution of FTO can be seen at higher irradiances when the current densities increase almost linearly with the electrode potential. Instead, the typical S-shaped behaviour of Fe<sub>2</sub>O<sub>3</sub> photoanodes is observed when using highly conductive substrates; however, it is also evident that photocurrent losses increase at higher potentials and irradiances. To better observe this effect, photocurrents were normalised by the irradiance (Fig. 4(b) and 4(d)).  $FTO|Fe_2O_3$ registers significant losses at higher irradiances, and photocurrents are almost 5 times lower than expected at 500 kW m<sup>-2</sup> when compared to photoanodes illuminated with 50 kW m<sup>-2</sup>. Hence, PEC cells operating under high photon fluxes are very susceptible to energetic losses not only associated with the photoelectrode materials and its properties, but also due to losses related with the design of the reactor. Furthermore, high-performance photoelectrode materials are expected to exacerbate these losses. In the case of  $Ti|Fe_2O_3$  (Fig. 4(d)), significant losses are also observed at intermediate electrode potentials due to different interdependent factors: current density distributions, ohmic



Fig. 3. Maximum temperature at different volumetric flows and irradiances for (a) FTO and (c) Ti substrates, and temperature profiles for a given volumetric flow,  $3.5 \text{ cm}^3 \text{ s}^{-1}$ , under an irradiance of 600 kW m<sup>-2</sup> for (b) FTO and (d) Ti substrates.



Fig. 4. Photocurrent densities as a function of applied electrode potential for (a) FTO and (c) Ti substrates; normalised photocurrents normalised by irradiance for (b) FTO and (d) Ti substrates, at different irradiances and  $3.5 \text{ cm}^3 \text{ s}^{-1}$ .

potential drop, bubble light attenuation, and improved charge transfer at higher temperatures. To decouple the effects of these factors on cell and material performance, the model was run under different conditions as specified in

#### Table 2

Summary of parameters used to decouple the contribution of different factors on device losses.

Case	Description	$\sigma_{\text{substrate}}$ [S m <sup>-1</sup> ]	$\sigma_l$ [S m <sup>-1</sup> ]	K <sub>b</sub>	$\phi_{g,\mathrm{surface}}$	${\xi_T \atop [K^{-1}]}$
1	Simplified model	10 <sup>9</sup>	300	0	0	0
2	+ Temperature effect on $\boldsymbol{\Phi}_{\text{bulk}}$	10 <sup>9</sup>	300	0	0	0.01461
3	+ Coverage and ohmic drop by bubbles	10 <sup>9</sup>	300	0	f(j)	0.01461
4	+ Light attenuation by bubbles	10 <sup>9</sup>	300	0.8	f(j)	0.01461
5	+ Ohmic drop in electrolyte	10 <sup>9</sup>	$\approx 20$	0.8	f(j)	0.01461
6	+ Ohmic drop in substrate (full model)	$\sigma_{\rm FTO,Ti}$	$\approx 20$	0.8	f(j)	0.01461



Fig. 5. Photocurrent densities for different the different cases (Table 2) for FTO and Ti substrates as a function of irradiance and applied electrode potentials of (a,c) 1.2 V and (b,d) 1.6 V vs. RHE.

Table 2. These effects were changed in a cumulative fashion starting from an simplified model: no ohmic drop across the substrate and electrolyte, no effect of the bubble on light attenuation and coverage of the electrochemical active area, and no temperature dependence of charge transfer in the bulk of the photoelectrode. Fig. 5 shows the predicted photocurrents for different scenarios at different irradiances and highlights the cause of the losses for each situation.

In the case of FTO|Fe<sub>2</sub>O<sub>3</sub>, Fig. 5(a) and 5(b), it is confirmed that the ohmic drop associated with substrate resistance is one of the main contributors of losses at higher electrode potentials. These results demonstrate the poor suitability of standard FTO as a substrate for highflux PEC application. However, this issue could be easily circumvented by deposition of highly conductive busbars (e.g. Ni, Au, etc.) on FTO to create a hybrid-substrate [30,52]. Ohmic losses in the electrolyte are also a major issue, especially at lower potentials and high irradiances for both types of substrates. The contrast between 1.2 and 1.6 V vs. RHE in Fig. 5 shows that the losses associated with light attenuation, area coverage, and ohmic drop due to bubbles are significant only at high current densities, i.e. when irradiances or electrode potentials are sufficiently high. For example, for Ti|Fe2O3 operating at 1.2 V vs. RHE, there are basically no losses associated with bubbles; the main cause of losses are current density distributions caused by ohmic drop in the electrolyte, which are in turn affected by the position of the counter and reference electrode.

In contrast, in the case of Ti $|Fe_2O_3$  operating at 1.6 V vs. RHE, the coverage of area and the ohmic drop resulting from the presence of

bubbles near the electrode surface are the main contributor of losses. In all cases, the light attenuation caused by bubbles is only a fraction of total losses, 7% in the worst scenario; however, this could be due to the good bubble management already implemented in the PEC cell and the relatively high volumetric flow. The gas fraction profiles (Fig. S8(c)), show that although there is a significant amount of bubbles near the surface, the optical path is almost free of bubbles because of the relatively high electrolyte velocity near the electrode's surface. In the absence of proper bubble management, optical losses could be as high as 28% [53] and 18% [54].

In the case of bubble coverage of an otherwise electroactive surface, the losses are mostly a function of the current density and the surface properties of the photoelectrode. Losses due to bubble coverage are only significant at high current densities (> 10 A  $m^{-2}$ ). Several models and mechanisms have been developed to predict the covered area; these depend on surface properties, redox couple, and hydrodynamic conditions, including micro- and macroconvection effects. Vogt et al. have developed numerous mechanisms for bubble coverage [35,55-57], notably, they found an exponential behaviour between the fraction of bubble coverage and log(*j*) after a large compilation of experimental studies [55]. It was found that ca. 10% of area coverage for 10<sup>2</sup> A  $m^{-2}$ , and 60% for 10<sup>4</sup> A  $m^{-2}$ . In our case, we assumed that the area covered by bubbles was equal to the volumetric fraction of bubbles at the electrode electrolyte interface, which is the worst case scenario in terms of losses due to bubble coverage. We found that for 600 kW m<sup>-2</sup> and 1.6 V vs. RHE, the modelled photoelectrode surface had an average



Fig. 6. Local photocurrent densities, surface temperature and fraction of available electroactive area for two different flow rates (2 and 5 cm<sup>3</sup>s<sup>-1</sup>) for Ti  $|Fe_2O_3|$  under an irradiance of 600 kW m<sup>-2</sup> at 1.6 V vs. RHE. Cases used in this figure refer to factors summarised in Table 2.

bubble coverage of *ca.* 20% and 5% for flow rates of 2 and 5 cm<sup>3</sup> s<sup>-1</sup>, respectively. The bubble coverage profiles for those flow rates can be seen in Fig. 6, together with the profiles of the temperature and local current densities.

When the resistivity of the substrate became negligible (case 5,  $\sigma_{\text{substrate}} = 10^9$  S m<sup>-1</sup>), the local current density remained unchanged compared to the full model (case 6) and shows a convex profile; this is in agreement with the relative position of the photoanode and cathode, where the latter has electroactive areas at the right and left edges of the illuminated area. However, when the electrolyte conductivity was increased and consequently the ohmic drop in the electrolyte became negligible (case 4), the current density profile changed to reflect the combined effects of surface temperature and bubble coverage, as can be seen in the lower part of Fig. 6, where higher temperatures and larger available electroactive areas  $(1 - \phi_g)$  increase the photocurrent density. After assuming that there is no light attenuation by bubbles (case 3), the current profile shifted further to higher values but kept a similar shape.

Once the effect of bubbles is fully disregarded (case 2), *i.e.*  $\phi_g = 0$ , the current density profile resembles almost exactly the temperature profile, which is expected as we assumed that  $\Phi_{\text{bulk}}$  is linearly dependent on temperature. Lastly, for the simplified model (case 1), *i.e.* in the absence of temperature effects and any other losses, there is an expected flat current profile across the illuminated area. These results show that even for small areas, 5 mm wide, there is a significant contribution of different factors toward the distribution of the current densities, and they should not be ignored when designing PEC cells and studying photoelectrode materials subjected to high photon fluxes.

Within the temperature window studied here, the effect of temperature on bulk charge transfer can significantly improve photocurrent densities, as it can be seen when comparing case 1 (simplified model) and case 2 ( $\Phi_{\text{bulk}} = f(T)$ ) in Figs. 5 and 6. This effect is more noticeable at higher irradiances as a result of increased temperature on the photoanode surface, and at higher electrode potentials when  $\boldsymbol{\Phi}_{\mathrm{surface}}$  is the highest. Strategies can be developed to take advantage of this synergetic effect to improve the overall performance of the cell. For this, the flow rate could be decreased and the electrolyte and photoelectrode temperature could be increased accordingly; however, these operating conditions must be carefully selected so as not to induce undesirable hot spots, increase the degradation rates of the photoelectrodes or promote accumulation of bubbles at the surface.

When comparing the results for two different flow rates, as shown in Fig. 6, it becomes evident that there are two competing mechanisms: bubble and surface temperature effect on the photocurrent density. For low flow rates (2 cm<sup>3</sup> s<sup>-1</sup>), the surface reaches higher temperatures, and consequently  $\Phi_{\text{bulk}}$  increases, as it can be seen for case 2; however, the available electroactive area decreases due to the presence of bubbles, which negatively impacts the photocurrent densities. In contrast, high flow rates (5 cm<sup>3</sup> s<sup>-1</sup>) remove bubbles faster from the surface, but the photoelectrode reaches lower temperatures as a result of improved convective effects. For the conditions presented here, 7.8% higher photocurrent densities were achieved when increasing flow rates from 2 to 5 cm<sup>3</sup> s<sup>-1</sup>; however, the aforementioned competing effects are highly dependent on the hydrodynamic conditions inside the cell and the properties of the semiconducting material.

#### 4.3. Experimental validation of the model

The predicted photocurrent densities were compared with the experimentally measured photocurrents obtained using a high flux PEC (HFPEC) cell. FTO $|Fe_2O_3$  was used as a photoanode and subjected to an irradiance of 140 kW m<sup>-2</sup>. A voltammogram at 10 mV s<sup>-1</sup> was used to measure photocurrents as a function of the applied electrode



**Fig. 7.** Experimental and predicted current densities as function of electrode potential for  $FTO|Fe_2O_3$  under 140 kW m<sup>-2</sup> and a flow rate of 3.5 cm<sup>3</sup> s<sup>-1</sup>. The predicted values corrected by ohmic drop correspond to the model when electrode and electrolyte conductivities are  $1 \times 10^9$  and 300 S m<sup>-1</sup>, respectively.

potential, and high-frequency electrochemical impedance spectroscopy was used to measure the ohmic resistance throughout the cell, which was found to be approximately  $R_s = 35 \ \Omega$ . The ohmic resistance was then used to correct the voltammograms [21]:  $E_{\text{corrected}} = E_{\text{applied}} - JR_s$ . This validation was only completed for FTO|Fe<sub>2</sub>O<sub>3</sub>, due to experimental challenges pertaining to the photoelectrochemical characterisation of Ti|Fe<sub>2</sub>O<sub>3</sub>, which underperformed due to a possible TiO<sub>2</sub> interlayer formed during annealing.

Fig. 7 compares the predicted values obtained with the model and the experimental values before and after correcting for the ohmic drop. The voltammograms in Fig. 7 show that the predicted values have a relatively low standard error of regression of 64.6 A m<sup>-2</sup>, and 73.0 A m<sup>-2</sup> when corrected by ohmic drop; it is worth noting that the photoelectrochemical characterisation used to collect the inputs for the model were obtained under low irradiances (1 kW m<sup>-2</sup>); therefore, the prediction at high irradiance is remarkably close to the experimental values, although there are still gaps that must be examined.

When the values are corrected for ohmic drop, the typical S-shape of the photocurrent densities is clearly seen in the predicted and measured values, although the S-shape is less defined for experimental values. This indicates that there are still factors in the model that are not accounted for to fully explain the photocurrent densities, especially at lower and higher potentials. This can be due to the temperature dependence of the equilibrium potentials, the kinetic rates, and the semiconductor properties, as explained in the limitations of the model in Section 2.7 and S7 in the Supporting Information. The earlier onset in experimental photocurrents might be due to a lowered equilibrium potential and a cathodic shift of the flat band potential. A more in-depth characterisation of photoelectrode materials operating at different temperatures is necessary to confirm this hypothesis. Future models will also include an estimate of the efficiency of gas evolution as a function of current density, as previously done in [29,35,56,58], and charge transfer efficiencies at the surface as a function of temperature.

The following sources of errors could lead to the observed mismatch between experimental and predicted photocurrent values: (*i*) the illuminated area might change depending on the irradiance and position of the cell due to the light source not being collimated, (*ii*) experimental current densities were extracted from voltammograms; therefore, the cell was not completely in steady state, (*iii*) the spectra of the HFSS lamp and the LED lamp were not the same, see Fig. S1; (*iv*) improved kinetics for dark currents at higher temperatures, and (*v*) the ohmic drop increases due to the presence of bubbles; this last effect was difficult to quantify experimentally and was not considered in the ohmic drop correction for the voltammograms, but it can be quantified and accounted for in the model.

#### 5. Conclusions

In this work, we present a multiphysics 2D model of a novel photoelectrochemical (PEC) cell used to study photoelectrode materials under high photon fluxes (i.e. concentrated irradiation). PEC devices operating under these conditions (50-600 kW m<sup>-2</sup>) are susceptible to energetic losses associated with their design; and although material properties are still a significant portion of the total losses, it is expected that high-performance photoelectrodes could exacerbate the losses attributed to current density distributions, ohmic drop, and bubble interference without judicious reactor engineering. Predicted photocurrent densities were compared with experimental measurements obtained using the high flux PEC cell. The results show that even for small areas, 5 mm wide, there is a significant contribution of different factors toward the distribution of the current density; these depend on surface and material properties, redox couple, hydrodynamic conditions, and thermal management. Furthermore, the simulations reveal that commercial FTO is not suitable due to significant ohmic losses under high flux. These results illustrate that highly conductive metallic substrates or FTO modified with current collecting metal busbars will be required for high flux PEC processes.

In summary, solar concentrated PEC is a promising research avenue to study due to potential benefits in the performance and scalability of reactor design, while allowing the surface of the photoelectrode to achieve higher surface temperatures, which could improve kinetic rates and charge transfer efficiencies of the semiconductor. The model proposed here could be useful to quantify energetic losses and decouple the different factors impacting the cell performance; this can be achieved by assessing the material properties and operating conditions when performing under high irradiances. This, in turn, could aid in the engineering and material selection of high flux PEC cells used for the production of solar fuels.

#### CRediT authorship contribution statement

**Franky E. Bedoya-Lora:** Conceptualization, Methodology, Software, Writing – original draft. **Isaac Holmes-Gentle:** Conceptualization, Methodology, Writing – original draft. **Sophia Haussener:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.electacta.2023.142703.

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