

IMPERIAL COLLEGE LONDON

**Photo-electrochemical
engineering of solar water
splitting devices**

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London

Declaration

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Photo-electrochemical engineering of solar water splitting devices

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Isaac Holmes-Gentle
October 2018

*'A quotation is a handy thing to have about,
saving one the trouble of thinking for oneself,
always a laborious business'*

A.A MILNE

Abstract

In order to scale up photo-electrochemical (PEC) water splitting, there are a number of engineering challenges that must be overcome. In order to logically approach this task, the PEC device was deconstructed into a classification framework comprising of two parts: the fundamental conceptual design and the engineering PEC device design. The first is used to investigate the fundamental limiting efficiencies of permutations of conceptual design, and the second to study the common elements of photo-electrode reactor design and critically compare examples from literature. After identifying the engineering challenges of scaling PEC devices, two specific issues were explored: 1) the optical losses from light scattered by bubbles at the gas-evolving photo-electrode under 'front side' illumination 2) the resistive losses in large area low conductivity substrate such as fluorine doped tin oxide (FTO). For both, the realistic losses were quantified and mitigation strategies evaluated. Finally, a new class of photo-electrochemical reactor was proposed: a membrane-less flow cell reactor that employs hydrodynamic separation of dissolved gaseous products. It is theoretically demonstrated that current densities typical of current PEC devices can be supported whilst suppressing bubble formation through operation at high pressure. The general operational design space was assessed with non-dimensional analysis and numerical modelling. Positive preliminary experimental results are displayed and a future work plan outlined. In summary, this thesis defines the role of photo-electrochemical engineering for solar to hydrogen devices, outlines the most pertinent challenges and begins to tackle a number of them, demonstrating that careful engineering design is required in order to realise any photo-electrochemical water splitting process.

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- [2] I. Holmes-Gentle *et al.*, “Assessing the Scalability of Low Conductivity Substrates for Photo-Electrodes *via* Modelling of Resistive Losses”, *Physical Chemistry Chemical Physics* **2018**, *20*, 12422–12429
- [3] I. Holmes-Gentle, K. Hellgardt, “A Versatile Open-Source Analysis of the Limiting Efficiency of Photo Electrochemical Water-Splitting”, *Scientific Reports* **2018**, *8*, DOI 10.1038/s41598-018-30959-9
- [4] I. Holmes-Gentle *et al.*, “Optical Losses at Gas Evolving Photoelectrodes: Implications for Photoelectrochemical Water Splitting”, *The Journal of Physical Chemistry C* **2018**, *123*, 17–28
- [5] I. Holmes-Gentle *et al.*, “Photoelectrochemical Reaction Engineering for Solar Fuels Production” in *Photoelectrochemical Solar Cells*, Advances in Solar Cell Materials and Storage 2, Scrivener-Wiley, **2018**

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Nomenclature and abbreviation

Notation

Symbol	Name/description	Units
a	Interfacial area per unit volume of the dispersion	m^2
a_b	Cross-sectional bubble area	m^2
a_s	Scattering cross-sectional area	m^2
A	Absorptance	-
A_{conc}	Geometrical area of the concentrating optics	m^2
$A_{electrode}$	Geometric electrode area	m^2
A_{photo}	Geometric photo-absorber area	m^2
A_{PE}	Photo-electrode geometric surface area	m^2
A_L	Area of incoming light before interaction with bubbles	m^2
$A_{membrane}$	Total area of membrane(s)	m^2
$A_b^{surface}$	Surface area of bubbles	m^2
AR	Aspect Ratio	-
b_i	Photon emissive flux from blackbody i which can be the sun (s), solar cell (e) or ambient surroundings (a)	$\text{s}^{-1} \text{m}^{-2} \text{J}^{-1}$
c	Speed of light	m s^{-1}
c_∞	Concentration of species i infinitely far from electrode surface	mol m^{-3}
c_i	Concentration of species i	mol m^{-3}
$c_{i,eq}$	Concentration of species i at equilibrium	mol m^{-3}
c_{ij}	Area concentration from node i to j	-
C	Irradiation concentration ratio	-
$C_{p,i,j}$	Molar heat capacity (const. pressure) of species i & phase j	$\text{J mol}^{-1} \text{K}^{-1}$

d_j	Thickness of j^{th} layer of stack	m
D_i	Diffusivity of species i	$\text{m}^2 \text{s}^{-1}$
e	Exponential constant	-
E	Electrode potential	V
E	Energy level	J
E	Electric field	V m^{-1}
E_o	Boundary electrode potential	V
E_λ	Spectral irradiance	W m^{-3}
E_{cell}°, E_{cell}	Electrochemical cell potential (standard conditions and non-standard resp.)	V
E_{eq}	Equilibrium electrode potential	V
E_g	Bandgap energy	
E_{red}°	Standard reduction potential of electrode anode E_{anode}° or cathode $E_{cathode}^\circ$	V
E_{rxn}	Absolute (positive) cell voltage	V
f	$= F/RT$	V^{-1}
f_B	Bubble evolution efficiency	-
f_g	Geometric factor for radiative emission	-
f_{ij}	Split fraction from node i to j	-
$f_{\text{optical loss}}$	Optical loss due to bubbles	-
F	Faraday constant	C mol^{-1}
F	Current concentration ratio	-
F_i	Geometric factor for blackbody i	-
g, g	Gravitational acceleration vector and constant at the surface of earth resp.	m s^{-1}
$\Delta G_{f, H_2}^\circ$	Standard Gibbs free energy of H_2 formation	J mol^{-1}
ΔG_{rxn}	Change in Gibbs free energy of reaction	J mol^{-1}
h	Planck constant	$\text{m}^2 \text{kg s}^{-1}$
h	Height of the frame	m
H_i^{cp}	Henry's constant of species i	$\text{mol m}^{-3} \text{Pa}^{-1}$
ΔH_{rxn}	Change in enthalpy of reaction	J mol^{-1}
ΔH_i^{vap}	Enthalpy of vaporisation for species i	J mol^{-1}

$\bar{\mathbf{I}}_{j,j+1}$	Interface matrix	-
I_{solar}	Solar irradiance power per area	$W\ m^{-2}$
$I_{T,system}$	Transmitted irradiance through experimental system	$W\ m^{-2}$
$\mathbf{j}$	Current density vector	$A\ m^{-2}$
j_o	Exchange current density	$A\ m^{-2}$
j_o	Dark saturation current (ideal diode eq.)	$A\ m^{-2}$
j_{abs}	Current density from absorption	$A\ m^{-2}$
j_{anode}	Anodic current density	$A\ m^{-2}$
j_{dark}	Dark current	$A\ m^{-2}$
$j_{electrode}$	Electrode current density	$A\ m^{-2}$
j_L	Photo-generated current (ideal diode eq.)	$A\ m^{-2}$
j_{lim}	Mass-transfer limiting current density	$A\ m^{-2}$
j_{photo}	Photo-electrode current density	$A\ m^{-2}$
j_{rad}	Current density from radiative recombination	$A\ m^{-2}$
k_B	Boltzmann constant	$m^2\ kg\ s^{-2}\ K^{-1}$
K_a	Total scattering coefficient	-
l	Path length of the light through dispersion	m
L	Square side length of substrate	m
$\bar{\mathbf{L}}_j$	Layer matrix	-
L_x	Channel width (normal to electrode plane)	m
L_y	Channel length (direction of flow)	m
$L_{y,electrode}$	Electrode length	m
L_z	Channel depth or substrate thickness	m
M	Membrane to electrode area ratio	-
$\mathbf{n}$	Unit normal vector	-
n_{b,O_2}	Number of moles in a single bubble of oxygen	mol
n_{e^-}	Electron stoichiometry in electrode reaction	-
$\dot{n}_i$	Molar flowrate of species i	$mol\ s^{-1}$
$\tilde{n}_j$	Complex refractive index of j^{th} layer of stack	-
$\dot{n}_{O_2}$	Molar flowrate of oxygen bubbles	$mol\ s^{-1}$
N_b	Number of bubbles per frame	-
N_{elec}	Number of pairs of electrolytic interfaces (electrolyser)	-

N_i	Flux of species i	$\text{mol m}^{-2} \text{s}^{-1}$
N_{photo}	Number of photo-absorbers	-
N_{RU}	Repeating units (efficiency model)	-
P	Pressure	Pa
P_0	Ambient pressure	Pa
P_{bias}	External bias power used	W
ΔP_{drop}	Pressure drop	Pa
P_{H_2O}	Vapour pressure of water in the bubble	Pa
P_j	Net optical power density	W m^{-2}
$P_j^{+/-}$	Optical power density of forward (+) and backward (-) travelling light	W m^{-2}
P_{other}	Other power added to system	W
P_{pump}	Pumping power	W
P_{solar}	Solar light power	W
Pe	Péclet number	-
q_e	Elementary positive charge	C
q_p^f, q_p^b	Spectral photon flux (front & back illumination resp.)	$\text{s}^{-1} \text{m}^{-3}$
Q	Reaction quotient	-
Q	Heat transferred to system	J
$\dot{Q}$	Volumetric flowrate	$\text{m}^3 \text{s}^{-1}$
$r^{+/-}, \bar{r}^{+/-}$	Complex reflection coefficients and intensity reflection coefficients from forward and backward travelling light resp.	-
R	Universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
$R^{+/-}$	Reflectance from forward and backward travelling light resp.	-
R_b	Bubble radius	m
$R_{bubbles}$	Reflectance of bubbles	-
R_D	Radius of integrating sphere input port	m
R_i	Reaction rate of species i	$\text{mol m}^{-3} \text{s}^{-1}$
$R_{i,electrode}$	Surface reaction rate of species i on electrode	$\text{mol m}^{-2} \text{s}^{-1}$
R_S	Radius of scattering cone	m
Re	Reynolds number	-

s_i	Stoichiometric coefficient of species i in electrode reaction	-
S	No. of suns	-
$\bar{S}$	System matrix	-
S_i	Supersaturation of species i	-
ΔS_{rxn}	Change in entropy due to reaction	J K^{-1}
t	Time	s
$t^{+/-}, \bar{t}^{+/-}$	Complex transmission coefficients and intensity transmission coefficients from forward and backward travelling light resp.	-
T	Temperature	K
T	Transmittance	-
$T^{+/-}$	Transmittance from forward and backward travelling light resp.	-
T_a	Absorber temperature	K
T_{amb}	Ambient temperature	K
$T_{bubbles}$	Transmittance through bubbles	-
T_s	Temperature of surface of sun	K
u_b	Bubble rise velocity	m s^{-1}
$\mathbf{u}, u_x, u_y$	Flow velocity vector, x component, y component resp.	m s^{-1}
U	Electric field intensity	$\text{V}^2 \text{m}^{-2}$
$U_{j,L/R}^{+/-}$	Electric field intensity of forward (+) or backward (-) propagating light on the left (L) or right (R) side of the j^{th} layer of the stack	$\text{V}^2 \text{m}^{-2}$
V_o	Overpotential	V
V	Potential difference	V
V_{total}	Total voltage for electrolysis	V
w	Width of the frame	m
W	Work done to system	J
z	Distance from the scattering event	m
α_a	Anodic charge transfer coefficient	-
α_c	Cathodic charge transfer coefficient	-

β_j	$= 2\pi d_j \tilde{n}_j / \lambda$ for j^{th}	-
γ	Bubble interface surface tension	N m^{-1}
Γ_Q	Current sources/sinks	A m^{-3}
δ	Boundary layer thickness	m
ϵ_0	Vacuum permittivity	F m^{-1}
η_a	Anodic overpotential	V
η_{APCE}	Absorbed photon-to-current conversion efficiency	-
η_c	Cathodic overpotential	V
η_{carnot}	Carnot efficiency	-
η_{coll}	Collection efficiency	-
$\eta_{coupling}$	PV-electrolyser coupling efficiency	-
η_{EC}	Electrolyser efficiency	-
η_{ETH}	Total input Energy-To-Hydrogen efficiency	-
η_f	Faradaic efficiency	-
η_{IPCE}	Incident photon-to-current conversion efficiency	-
η_{pump}	Pump efficiency	-
η_{PV}	Photo-voltaic efficiency	-
η_{STF}	Solar to hydrogen efficiency	-
η_{STH}	Solar to hydrogen efficiency	-
θ_S	Scattering angle	rad
κ	Electrolyte conductivity	S m^{-1}
λ	Wavelength	m
$\mu, \mu_{l/g}$	Dynamic viscosity (l = liquid, g = gas)	Pa s
$\Delta\mu$	Chemical potential	J mol^{-1}
$\xi_{light/dark}$	Photo-diode signal (light or dark)	V
ρ	Substrate bulk resistivity	$\Omega \text{ m}$
$\rho, \rho_{l/g}$	Fluid density (l = liquid, g = gas)	kg m^{-3}
σ	Substrate conductivity	S m^{-1}
φ_{H_2}	Molar H_2 production rate	mol s^{-1}
$\varphi_{H_2}^{\text{cathode}}$	Molar H_2 production rate at the cathode	mol s^{-1}
$\varphi_{H_2, \text{outlet}}^{\text{side/total}}$	Molar H_2 production rate at outlet where the portion of outlet considered is one side of the reactor (cathodic or anodic) or the total outlet	mol s^{-1}

Φ	Electric potential	V
Φ_o	Boundary electric potential	V
$\Phi_{electrolyte}$	Electrolyte electric potential	V
ψ	Optical acceptance factor	-

Abbreviations

Abbreviation	Name/description
AM1.5G	ASTM International for the standard terrestrial solar spectrum
APCE	Absorbed photon to current efficiency
CAD	Computer aided design
EC	Electrolyser (Electrochemical cell)
ETH	Total input energy to hydrogen
EtOH	Ethanol
FTO	Fluorine doped tin oxide
HER	Hydrogen evolution reaction
IPCE	Incident photon to current efficiency
LED	Light emitting diode
OER	Oxygen evolution reaction
PEC	Photo-electrochemical cell
PV	Photo-voltaic
STF	Solar to fuel
STH	Solar to hydrogen
TCO	Transparent conductive oxide

Chapter 1

Introduction

It could be argued that one of the greatest challenges that humanity currently faces is the reduction of global fossil fuel usage and a transition to a more immediately sustainable energy cycle, whilst meeting the constantly increasing demand for energy. In this chapter, the challenges of renewable energy and energy storage are outlined. Solar energy conversion to fuel, such as hydrogen, is discussed as one solution to the issue of energy storage. Finally, the structure of the thesis is outlined.



Credit: NASA Goddard, 2012, "Black Marble - Americas",
NASA ID: GSFC_20171208_Archive_e001587

1.1 Energy, sustainability and fossil fuels

The energy demands of modern society are currently unsustainable. Fuelled by both population and economic growth, the world's energy consumption is rising and is currently predominantly met through the burning of fossil fuel to release the stored chemical energy in order to do work (*e.g* kinetic, heat, electrical, *etc.*). This vast natural resource of coal, oil and gas is formed from the thermal decomposition of organic matter over millions of years, and therefore ultimately derives from solar energy captured by photosynthesis. Whilst photosynthesis constitutes a solar to fuel process on the grandest of scales, the rate of consumption of fossil fuel *versus* the rate of formation of these resources is not sustainable. The combustion of fossil fuel is renewable only if it is consumed at such an insignificant rate as to render it meaningless in fulfilling the global demand for energy.

As this carbon cycle is unbalanced, fossil fuels are therefore a finite resource and it could be argued that such a precious resource should be depleted carefully due to its importance in a large number of chemical feedstocks. But perhaps more important than this, is the imbalance that burning fossil fuel causes to the carbon cycle and the vast amounts of CO_2 being released into the atmosphere (see Figure 1.1). This has resulted in an increase in CO_2 concentrations from approximately ~ 280 ppm in the 1800s to over 400 ppm now. It now seems certain that human activity and fossil fuel consumption have disrupted the balance of the Earth's atmosphere, leading to climate change [6]. A study by McGlade and Ekins estimated that 'a third of oil reserves, half of gas reserves and over 80 percent of current coal reserves should remain unused' in order to stop a 2°C rise in global temperatures [7].

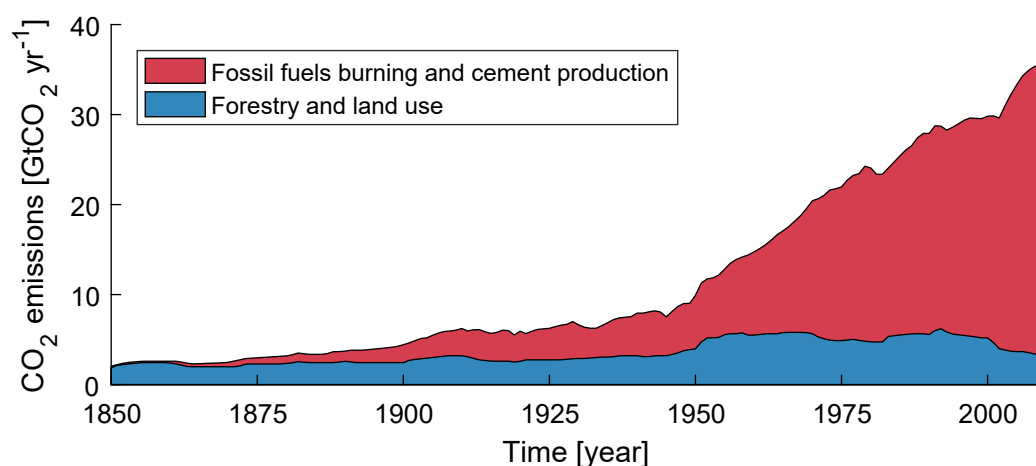


Figure 1.1: Global anthropogenic CO_2 emissions (adapted from IPCC [6])

Furthermore, the pressure on energy resources is only increasing as the human population grows. Figure 1.2 shows both the breakdown of the world energy consumption

by the primary energy source and the growth in human population. This shows that presently, non-renewable fossil fuels continue to be our predominant primary energy source [8]. As energy availability is irrevocably interlinked to food, water and human development, the utilisation of cheap and abundant fossil fuel resources has enabled the growth of human population to a scale past which it feasible to be supported by sustainable traditional biofuel.

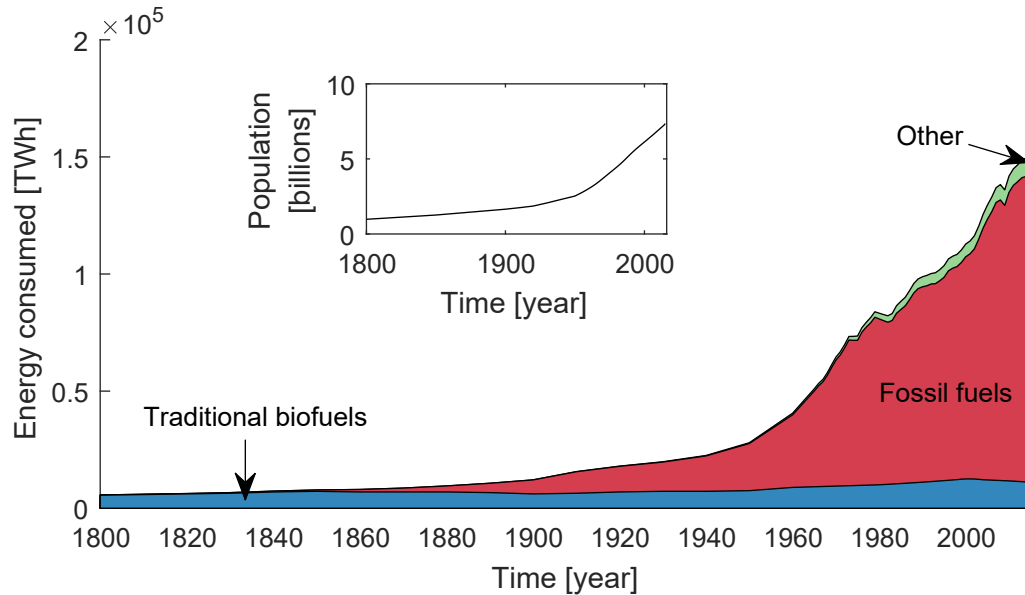


Figure 1.2: Historical energy consumption by primary energy source with inset graph showing world population growth over the same timescale (primary energy consumption data taken from [9–11], and for global population from Ref. [12, 13])

In light of the current social and political pressures to move towards a more immediately sustainable future, there is a great global effort into researching the future of an energy market that does not rely on fossil fuels.

1.2 Renewable energy, solar energy and energy storage

There are many alternative primary energy sources such as: solar, wind, tide, wave, hydroelectric and each comes with their respective advantages and disadvantages. The overarching difficulty with all renewable sources is meeting all three of the following conditions: A constant and predictable supply of energy, a large enough energy resource and a high energy density. Figure 1.3 shows the total extractable power of the renewable energy source against the supply in 2017 and the feasible technical limit. It is evident that the total solar energy reaching the surface of the earth is immense at roughly 120,000 TW, when compared to the total world energy consumption by humanity of roughly 15-20 TW. However, the solar resource is diffuse and hence in order to meet

energy demand, the required area of solar energy capture devices will be monumental. For example, demand can be met by covering approximately 0.16% (820,000 km²) of the earth's surface with 10% efficient solar cells [14].

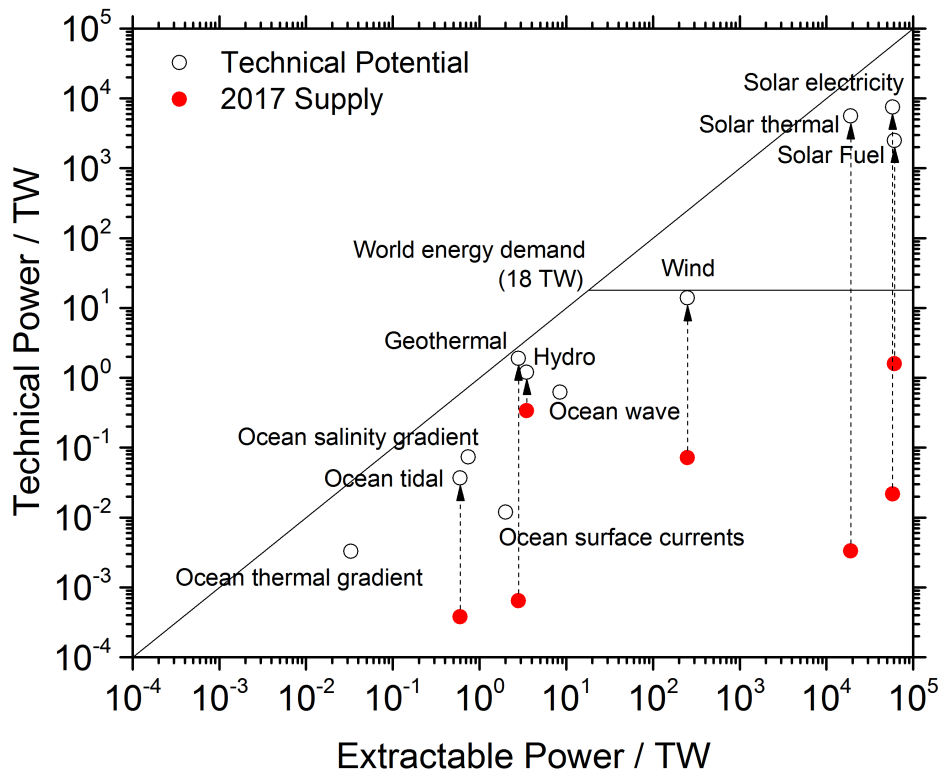


Figure 1.3: Extractable power against technical potential for different renewable technologies [5] (adapted from Tsao *et al.* [15] with updated values)

Another significant challenge is that the solar resource is intermittent and unpredictable on an hourly, daily, monthly basis (*e.g.* clouds, day and night, seasons respectively). This is further complicated by the issue that the demand for energy also fluctuates with time. Matching renewable supply to energy demand, is a significant limitation of intermittent power sources which will ultimately limit their penetration into the energy market. Without an economically viable way to bridge the gap between supply and demand, the energy market relies on fossil fuel burning technologies (such as gas fired power stations) to overcome this imbalance.

Furthermore, the storage of energy is necessary for our transportation systems. This is especially true for energy intensive transport modes which travel great distances between refuelling such as planes and ships. There are only a handful of prototype fully electric aeroplanes, and such technology is currently unfeasible for commercial flights [16].

The solution to the challenge of using intermittent renewables to meet an intermittent

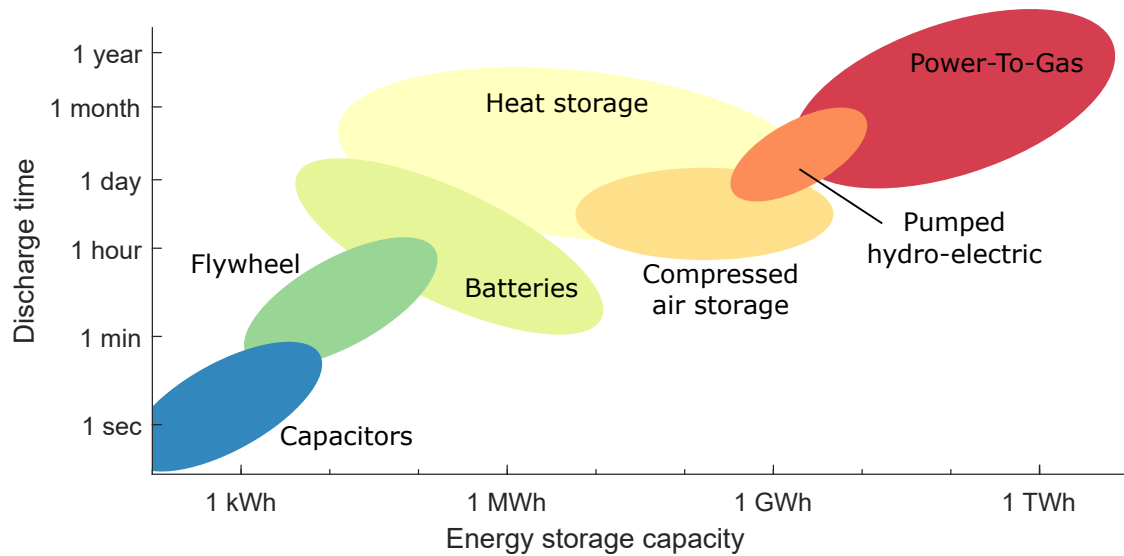


Figure 1.4: Overview of various energy storage technologies based on representative ranges based on prospective technologies for energy capacity and discharge time. Adapted from Sterner and Stadler [17] and World Energy Council [18]

and independent energy demand, is therefore energy storage. There are a multitude of energy storage technologies which could be employed for grid level storage, such as pumped hydro-electric, compressed air storage, liquid air storage, flywheels, flow batteries, capacitors, pumped heat electrical storage or batteries (Li-Ion, Ni-Cd, Ni-MH *etc.*) to name a few [19, 20]. Figure 1.4 shows the approximate position of prospective technologies with respect to discharge time and storage capacity and is comparable to Fig. 12 (discharge time *vs.* rated power) in Ref. [20]. There are fewer energy storage options when long term storage and large capacity is required, where pumped hydro-electric, which stores gravitational potential energy, is a mature and widely implemented energy storage technology. A more prospective technology is power-to-gas/fuel which stores energy as chemical potential energy and has the potential to store vast quantities of energy and is less geographically constrained. Furthermore, distributed systems, such as transportation and for systems requiring a high power to volume and/or weight ratio (*e.g.* commercial aircraft), may require energy stored as a fuel.

Therefore, if the reliance on fossil fuels is to be curbed, without an unimaginable shift in energy use, the implementation of a sustainable chemical fuel cycle is required alongside the use of other energy storage technologies. The solar energy resource available is immense and dwarfs the projected energy demand, and therefore is the ideal primary energy source for a fuel generating process [21]. A solar to fuel process would potentially advance the degree to which solar energy can be used to meet demand, as the storage of solar energy is one of the main technological factors limiting its implementation [22].

1.3 Solar fuels

Globally, there is a substantial amount of research underway to develop an economically viable process to convert solar energy directly into fuels [22–24] and this could be an approach to produce zero carbon emission transportation fuels [21, 25]. There are a number of conceptual routes to producing a fuel and Figure 1.5 shows each pathway between energy types with the name of the conversion technology.

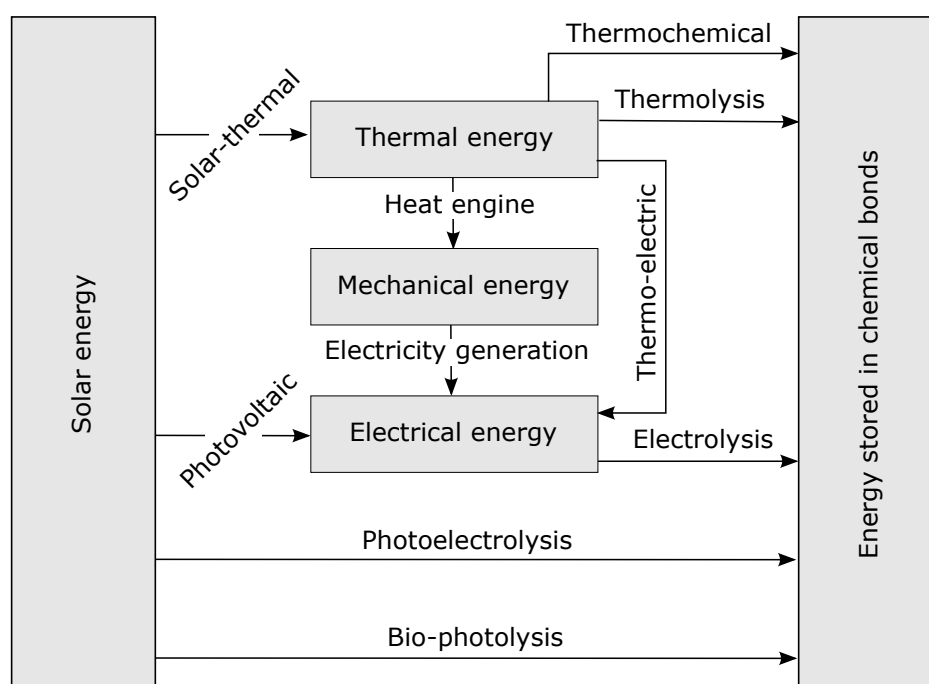


Figure 1.5: Energetic pathways to solar derived fuels

The most well-researched solar fuel is hydrogen and the concept of using it as an energy vector, commonly termed as a “hydrogen economy”, is an established field with a long history dating back to 1968 [26]. Hydrogen can be generated in many ways, from the electrolysis of water (renewable or nuclear electricity sources) to the reforming of natural gas and hence is a versatile energy carrier [27]. The hydrogen cycle is noted for its low toxicity as the final product is water [28].

However, hydrogen’s gaseous nature leads to significant problems with storage, though it is important to note the large scale storage of hydrogen is still cheaper than that of electricity [25]. This has been overcome by further chemical reactions to produce hydrogen-derived fuels such as methanol or methane and hydrocarbons such as petrol from syngas ($\text{H}_2 + \text{CO}$). These fuels are more realisable in today’s market, as the current installed global infrastructure caters for an economy based on liquid hydrocarbon fuels and natural gas.

The technoeconomics of solar fuel production is very challenging [29] and could be

seen as the main impediment to the implementation of these systems. However, the economic feasibility is driven by market competition with fossil fuels, and therefore regulation, political choices and public perception play a significant role in the economics. And therefore, it is arguable that the challenge is not just how to achieve a solar to fuel process that can rival the economic efficiency of fossil fuels, but how to reduce energy usage per person and to determine the cost of energy not only through market forces but by factoring in some environmental cost (*e.g.* an emissions trading scheme, governmental taxation and regulation on fossil fuel usage *etc.*).

1.4 Review of solar hydrogen generation technologies

This thesis will be focused on the generation of arguably the simplest solar fuel: hydrogen. Currently, hydrogen is produced mainly from fossil fuels (99% [27]) through processes such as natural gas reforming, hydrocarbon partial oxidisation and coal gasification. For a hydrogen economy to be sustainable, there has been much research into converting the sun's energy into the chemical energy stored in hydrogen. The main technological pathways for converting solar energy to hydrogen are outlined in Table 1.1 along with their respective advantages and disadvantages.

Photo-electrochemical water splitting is one promising pathway to solar fuels, but whilst there are a number of reported laboratory scale demonstration [30], there still exists obstacles to large scale implementation and commercialisation [14, 31, 32]. To put this in context of the economic challenge, hydrogen production using conventional steam reforming technologies with gas and coal feedstock result in a hydrogen price of \$1.2-\$1.8 per kg H₂ (updated estimate adapted from Lemus and Martínez Duart [33]). Conversely, predicted hydrogen prices for photo-electrochemical systems range from \$1.60 to \$11.4 per kg H₂ [31, 34], although the uncertainty in these estimates will be high due to the low technology readiness level of PEC. For a similar but more established technology of PV + electrolysis, Shaner *et al.* [34] estimated a value of \$12.1 per kg H₂. Clearly, in order for hydrogen production from photo-electrochemical water splitting to be feasible both a reduction in estimated cost and an increase in the technology readiness level will be required. Therefore, the photo-electrochemical engineering of solar water splitting devices is necessary alongside more fundamental scientific endeavours such as improvements in materials and a superior understanding of the underlying mechanisms.

Table 1.1: Pathways to hydrogen production from solar energy

Thermolysis	Solar-thermal electricity + Electrolysis	Photoelectrolysis	Biophotolysis
Thermal decomposition of water. Requires highly concentrated solar energy as the temperature required to obtain significant levels of dissociation are greater than 2200 K [35] • Uneconomical [35–37] • Low overall efficiencies [27] • Material stability issues [38] • Product separation issues [35]	Solar-thermal electricity converts a temperature difference into mechanical energy through a heat engine. This mechanical energy can be used to generate electricity which is used to electrolyse water • Solar thermal technology has been proven on a large scale in high solar power locations (e.g Spain) [39] • Use of conventional technologies such as rankine cycle [39] • Not suitable for distributed hydrogen generation or high latitudes • Good solar-to-hydrogen efficiencies [40]	A system in which the semiconductor, which absorbs the light leading to a photo-excitation, is in direct contact with the electrolyte. The current generated from the separated photo-excitation drives the electrolysis of water. • Potentially high theoretical efficiencies [41–43] • Inherently easy separation of hydrogen and oxygen if membrane is used [14] • No suitable material has yet been found to realise both inexpensive and bias-free water splitting [14]	The modification of algae to produce hydrogen as a by-product of photosynthesis • Significantly better efficiency than photosynthesis in trees and plants [44] • Hydrogen production from algae is currently at a lab scale [27] • Low overall efficiencies lead to large area of algae required
Thermochemical	PV + Electrolysis	Biomass conversion	Artificial photosynthesis
A reaction cycle that uses highly concentrated solar energy as the heat source for the reactions. The most favourable cycles are metal oxide redox pair cycles such as ZnO/Zn [35]. Thermochemical cycles were originally developed for waste heat from a nuclear reactor [21] • Requires extremely high concentration of sunlight leading to scale-down issues • Easy separation of H₂ and O₂ [37] • Significant uncertainty in the technical and economic aspects [27, 35, 45, 46]	A separate standalone electrolyser is coupled to a photo-voltaic solar cell both of which are mature technologies • Massive and expanding current market for PV [28] • Currently not competitive enough [47] but as cost of PV and electrolyser technology reduces, it may be economically viable in the future [21, 45, 48]. • High solar-to-hydrogen efficiency is achievable with current technology [43, 49] • Modular nature means that each component can be optimised separately and hydrogen can be advantageously produced at pressure with existing technology • Solar power variability leads to non-optimal performance (over designed electrolyzers in low irradiation) • High overpotentials in electrolyser due to large current densities [14]	The conversion of light to natural sugars <i>via</i> photosynthesis by organisms can be harnessed in order to produce hydrogen. Biomass (from plants, algae <i>etc.</i>) can be converted to hydrogen through gasification • Low overall efficiency of photosynthesis in trees and plants (>1%) [44] and therefore requires incredibly large areas and may compete with food production [50]. However it can also be a by-product of food farming (e.g sugar cane) • Conversion of biomass is well-researched and technologically feasible [21]	Use of synthetic biology to mimic the complex and efficient reactions of PSII (photosystem II) which is the water splitting reaction in photosynthesis. • Theoretically better efficiency than biophotolysis utilising the selectivity and efficiency of enzymes [51] • Currently low efficiencies and stability issues [51, 52]

1.5 Photo-electrochemical water splitting

The photo-voltaic effect was first reported using a semiconductor-electrolyte junction, rather than with a solid state semiconductor-semiconductor junction. In 1839, Becquerel described a silver chloride electrode producing current and voltage through light illumination [53]. The first demonstration of water splitting using a photo-electrochemical device came in 1972, with Fujishima and Honda [54] who described the performance of a TiO_2 photo-anode and discussed its application to water splitting. Since this seminal work, there has been significant research into PEC water splitting resulting in significant breakthroughs in device performance [30].

However, to date photo-electrochemical water splitting remains almost exclusively an academic concern and has been constrained from commercialisation by several technological and economic challenges. The technical challenges in particular will be discussed in detail in the following chapters.

1.6 Goals and structure of this thesis

Given the present circumstances in the field of photo-electrochemical water splitting, the engineering challenges inherent in PEC devices must be quantified and overcome/circumvented. Therefore, this thesis aims to address the photo-electrochemical engineering aspects of PEC devices. An overview of the chapters can be found in Figure 1.6. Firstly, the PEC device is systematically deconstructed in order to understand both the limiting thermodynamics and the scale-up challenges. From this, a number of issues can then be tackled: namely the interaction of light with bubbles evolving from the photo-electrode surface and the effect of the substrate resistivity on the device performance. Finally, a new class of PEC reactor design is proposed: membrane-less product separation *via* forced laminar convection. This design is studied theoretically and preliminary experimental results are given.

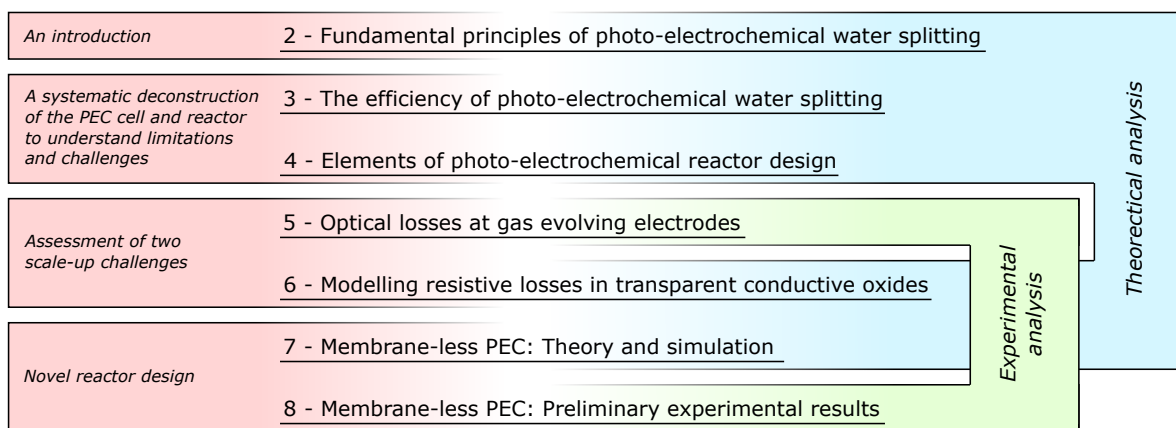
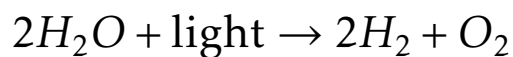


Figure 1.6: Overview of thesis structure. Here, each chapter (central column) is grouped by its common themes (left column) and whether the analysis was theoretical or experimental (right column).

Chapter 2

Fundamentals of photo-electrochemical water splitting

This chapter introduces the fundamental principles behind photo-electrochemical water splitting, briefly detailing the most salient underlying scientific theories. This chapter aims to outline key terminology and define the photo-electrochemical performance metrics along with a description of typical PEC experiments.



2.1 The electrochemical cell and electrolysis of water

An electrochemical reaction occurs at an electrode, where the chemical reaction occurring at the interface liberates or consumes electrons through the transformation of chemical structure. These electrons are transferred (*i.e.* electric current flows) either from the reactants to the electrode (oxidation) or from the electrode to the reactants (reduction). For any appreciable current to flow, the reduction reaction must be matched to an oxidation reaction so the rate of electrons liberated equals rate of electrons consumed. This simultaneous oxidation and reduction occurs at the anode and cathode of an electrochemical cell. Both electrodes are connected *via* an electronic pathway (*i.e.* *via* an electronic conductor such as a metal) and an ionic pathway (*i.e.* *via* an ionic conductor called an electrolyte). Electrochemical cells fall into two categories: galvanic and electrolytic cells, based on the overall spontaneity of electrochemical reactions. Galvanic cells release energy (*e.g.* batteries, fuel cells) and so the change in Gibbs energy is negative $\Delta G_{rxn} < 0$, whereas electrolytic cells require input energy to drive the electrochemical reaction (*e.g.* electrolysis of water) and hence the change in the Gibbs energy is positive $\Delta G_{rxn} > 0$. The Gibbs free energy of the reaction can be related to the electrochemical cell potential by Eq. (2.1).

$$\Delta G_{rxn} = -n_e F E_{cell} \quad (2.1)$$

Here, the standard cell potential is defined as Eq. (2.2) where E_{anode}° and $E_{cathode}^\circ$ are the standard reduction potential (E_{red}°) of that electrochemical reaction at the anode and cathode respectively.

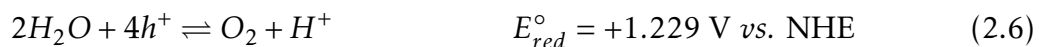
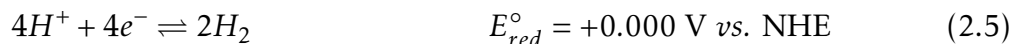
$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ \quad (2.2)$$

Water electrolysis is the decomposition of water into hydrogen and oxygen in an electrochemical cell. Therefore, the overall reaction $2H_2O \rightarrow 2H_2 + O_2$ can be divided into oxidation (oxygen evolution reaction) and reduction (hydrogen evolution reaction) half-reactions which depend on the pH of the electrolyte. The two equation sets are interchangeable with the equation for the self-ionisation of water: $H_2O \rightleftharpoons H^+ + OH^-$

For alkaline electrolytes:



For acidic electrolytes:



The standard cell potential E_{cell}° of the water splitting cell is therefore -1.23 V which corresponds to a positive ΔG_{rxn} and is therefore not spontaneous. This assumes heat from the surrounding is supplied to the reaction, and if the system considered is adiabatic, the required voltage becomes -1.48 V and is termed the thermoneutral electric potential. The standard cell potential is independent of pH as both half-reactions are dependent on pH in the same manner: -59 mV per positive unit pH change. This can be derived from the Nernst equation given in Eq. (2.7).

$$E_{red} = E_{red}^\circ - \frac{RT}{n_e F} \ln(Q) \quad (2.7)$$

The reversible thermodynamic minimum energy required will therefore be 237 kJ mol⁻¹ supplied as electrical energy which corresponds to a potential difference of -1.23 V. However, unavoidable kinetic losses will mean a potential difference greater than this is necessary to drive the electrolysis reaction. This extra electric potential required, namely the over-potential V_o , will have to be supplied in addition to the thermodynamic potential difference externally by an electric power source.

2.2 The solar resource

The sun is earth's closest star and without the solar energy travelling to earth in the form of electromagnetic radiation (*i.e.* sunlight), there would be no life (as we know it) on earth. The sun is composed of hot plasma which derives its thermal energy from fusion, and it is this temperature which causes it to radiate light. The sun can be approximated as a black body at roughly 6000 K which will emit radiation according to Planck's law given in Eq. (2.8). In actuality, the terrestrial solar spectrum contains notable features caused by interaction with the atmosphere, such as absorption and scattering of light. As the solar spectrum is both spatially and temporally dependant, a standard was created by ASTM International for the standard terrestrial solar spectrum: AM1.5G [55]. This AM1.5G solar spectrum is plotted in Figure 2.1, and assumes an air mass of 1.5, a 37° tilted surface, capture of the global spectrum (all the light including diffuse) and was developed from data taken from typical US locations and adjusted so that the total power is 1000 W/m² for use as an idealised standard.

$$E_\lambda = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{k_B T}} - 1} \quad (2.8)$$

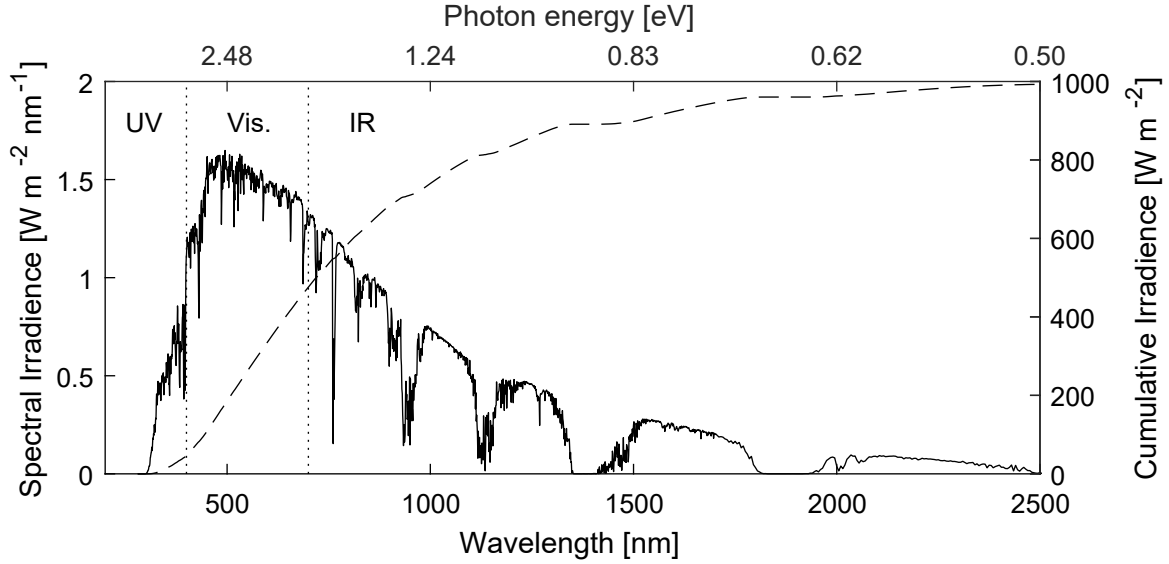


Figure 2.1: Standard solar spectrum (AM1.5G) showing both the spectral irradiance and the cumulative irradiance

2.3 Photo-electrochemical water splitting

As mentioned previously, electrolysis of water under standard conditions requires at the very least 1.23 V of electrical energy. If this energy is supplied by converting light to electrical potential, the process can then be termed photo-electrochemical (PEC) water splitting. Such a PEC device can convert solar energy to stored chemical fuel which could theoretically create a sustainable fuel cycle, as mentioned in Chapter 1.

Photo-electrochemical water splitting employs a quantum solar energy conversion device, which an electron absorbs an incoming photon resulting in an excited electron state. This photo-excitation promotes an electron from the valence band to the conduction band of the semiconductor which results in an excited electron and a hole pair, where a so-called hole is the absence of an electron in the valence band. Next, charge separation typically occurs by carriers migrating in the electric field formed in the semiconductor by the semiconductor-electrolyte interface, commonly called the depletion layer or space charge layer. In a photo-electrode, the minority carriers are transported to the electrochemical interface in order to drive the reaction. For a photo-anode, holes oxidise water, and for a photo-cathode electrons reduce water at the surface. The opposite charge carrier (majority carriers) are collected *via* an electronic

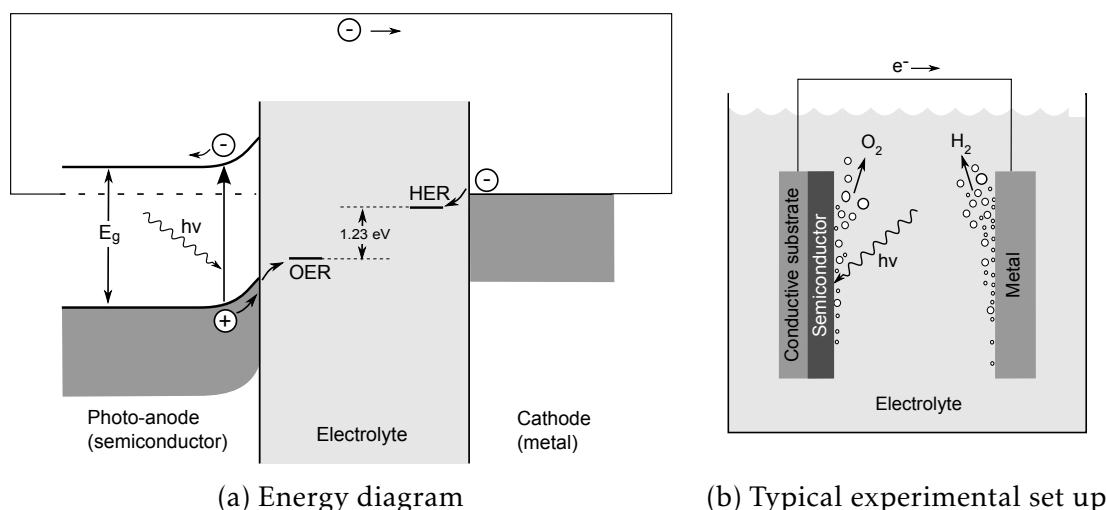


Figure 2.2: Diagrams of a simple photo-anode PEC water splitting where the energy of the incoming photon is written as $h\nu$ where h is the Planck constant and ν is the photon frequency

conductor and transported to the opposite electrode. Photo-excitations that are not successfully separated will recombine and is a major loss pathway for inexpensive sub-optimal materials such as metal oxides.

An example of a photo-electrochemical water splitting system with a single n-type semiconductor photo-anode can be seen in Figure 2.2. Figure 2.2a displays the energy diagram showing the location and transport of the excited electron and hole, where the higher the electron is in the diagram, the greater the energy of the electron (which corresponds to a more negative electric potential). Figure 2.2b, shows how this system would typically be physically constructed, with two mono-polar electrodes connected by a wire. In Chapter 4, a discussion and literature review on the possible PEC reactor design is given.

In order to split water under standard conditions, a single material PEC cell would require a bandgap higher than 1.23 eV due to the unavoidable entropic losses. Chapter 3 investigates these fundamental limits in detail and it is shown a minimum bandgap of *ca.* 1.5 eV is necessitated. In reality, if the kinetic losses (*i.e.* the overpotential required for current to flow) are considered for HER and particularly OER, a 1.6-2.4 V potential is required to split water [56, 57] leading to a larger photo-voltage and hence bandgap for a single absorber device. As the incident photon must possess energy greater than the band gap for photo-excitation to occur, only a portion of the solar radiation will be absorbed. Furthermore, if the photon has more energy than the bandgap, the above bandgap energy will be lost as the excited electrons will thermalise down to the conduction band edge. Therefore, in order to match the solar spectrum to the required electric potential generated whilst reducing thermalisation losses and the proportion of sub-bandgap photons, multijunctions devices have been investigated and

all experimental demonstrations to date, which demonstrate an appreciable efficiency, employ this approach [30].

2.4 Performance metrics

The performance of a PEC device can be quantified by the following metrics. The solar-to-hydrogen (STH) efficiency is given in Eq. (2.9) and is the fraction of energy stored that can subsequently be extracted as work (hence the Gibbs energy) to the total solar power input. Here, φ_{H_2} is the formation rate of H_2 , $\Delta G_{f,H_2}^\circ$ is the Gibbs free energy of H_2 formation, P_{solar} is the total power of the sunlight and I_{solar} is the irradiance power per area of the sunlight. Assuming the products are successfully collected, the STH efficiency can also be written in terms of the photocurrent j_{photo} and the thermodynamic cell voltage required to drive the reaction E_{rxn} (*i.e.* 1.23 V under standard conditions) and the H_2 evolution faradaic efficiency η_f . It is important to note that the STH efficiency can also be defined using the enthalpy of reaction $\Delta H_{f,H_2}^\circ$ rather than the Gibbs energy and so care must be taken when interpreting efficiencies stated in literature.

$$\eta_{STH} = \frac{\varphi_{H_2} \Delta G_{f,H_2}^\circ}{P_{solar}} = \frac{j_{photo} E_{rxn} \eta_f}{I_{solar}} \quad (2.9)$$

Another important performance metric focuses on the fraction of incident photons successfully captured and converted to current. The incident photon-to-current conversion efficiency (IPCE) or external quantum efficiency is given in (2.10) where h , c , q is Planck's constant, speed of light and the fundamental charge respectively.

$$\eta_{IPCE}(\lambda) = \frac{hc}{q_e} \left(\frac{j_{photo}(\lambda)}{\lambda I_{solar}(\lambda)} \right) \quad (2.10)$$

The absorbed photon-to-current conversion efficiency (APCE) or internal quantum efficiency is related to the IPCE with Eq. (2.11) by the absorptance A . It is defined as the fraction of absorbed photons that are successfully converted to current.

$$\eta_{APCE}(\lambda) = \frac{IPCE(\lambda)}{A(\lambda)} \quad (2.11)$$

Solar energy conversion to power/fuel is ultimately a type of heat engine, which operates on the temperature difference between the sun and the earth. A '1st law' efficiency for any energy conversion process can be defined as the ratio of the power converted/stored to the input power Eq. (2.12). The solar-to-hydrogen efficiency is

equal to the 1st law efficiency if the source of power to the device is only from solar irradiance (*i.e.* no ancillaries, such as pumps, that consume mains electricity) [58].

$$\eta_{1^{\text{st}} \text{ law}} = \frac{P_{\text{converted}}}{P_{\text{input}}} \quad (2.12)$$

A 2nd law efficiency, or exergy efficiency, is a commonly used metric [59, 60] in order to compare the process with the theoretical maximum efficiency for any heat engine: the Carnot cycle ($\eta_{\text{max}} = 1 - T_{\text{cold}}/T_{\text{hot}}$). This metric, given in Eq. (2.13), is particularly useful in comparing different heat engines with various hot and cold sink temperatures.

$$\eta_{2^{\text{nd}} \text{ law}} = \frac{\eta_{1^{\text{st}} \text{ law}}}{\eta_{\text{max}}} \quad (2.13)$$

The 1st law efficiency could be compared with other definitions for a maximum efficiency that takes into account realistic non-idealities such as a finite heat source/sink which changes temperature as heat is transferred [60]. In a similar manner, a metric comparable to the exergy efficiency could be devised for solar to fuel devices where instead of dividing the 1st law efficiency with the Carnot efficiency, the STH efficiency will be divided by the ‘Shockley–Queisser’ limit. This is a more realistic thermodynamic maximum for solar energy conversion devices as it takes into account the unavoidable deviations from the ideal Carnot efficiency, taking into account the mechanism of energy conversion [61]. This proposed metric will be discussed in greater detail for example systems in Chapter 3.

2.5 Common PEC experiments

In this section a brief overview of typical photo-electrochemical experiments are given. Firstly, all photo-electrochemistry experiments will require a cell which contains the photo-electrodes(s), electrode(s) and electrolyte. For external measurement of the electrode potentials and currents flowing, a potentiostat or galvanostat is connected *via* wires to the relevant components. For a three probe electrochemistry experiment, the electrochemistry at the working electrode is investigated *versus* the electrode potential given at a reference electrode, by controlling the current to the counter electrode. This set-up can be seen in Figure 2.3c and a photograph of a self designed PEC three probe measurement cell can be seen in Figure 2.4.

In order to conduct a photo-electrochemical experiment, light must be provided to the relevant components of the cell such as the photo-electrode. Two common light sources for experiments are shown in Figure 2.3a and 2.3b, for broadband and monochromatic light respectively. STH efficiency is commonly calculated through experiments using

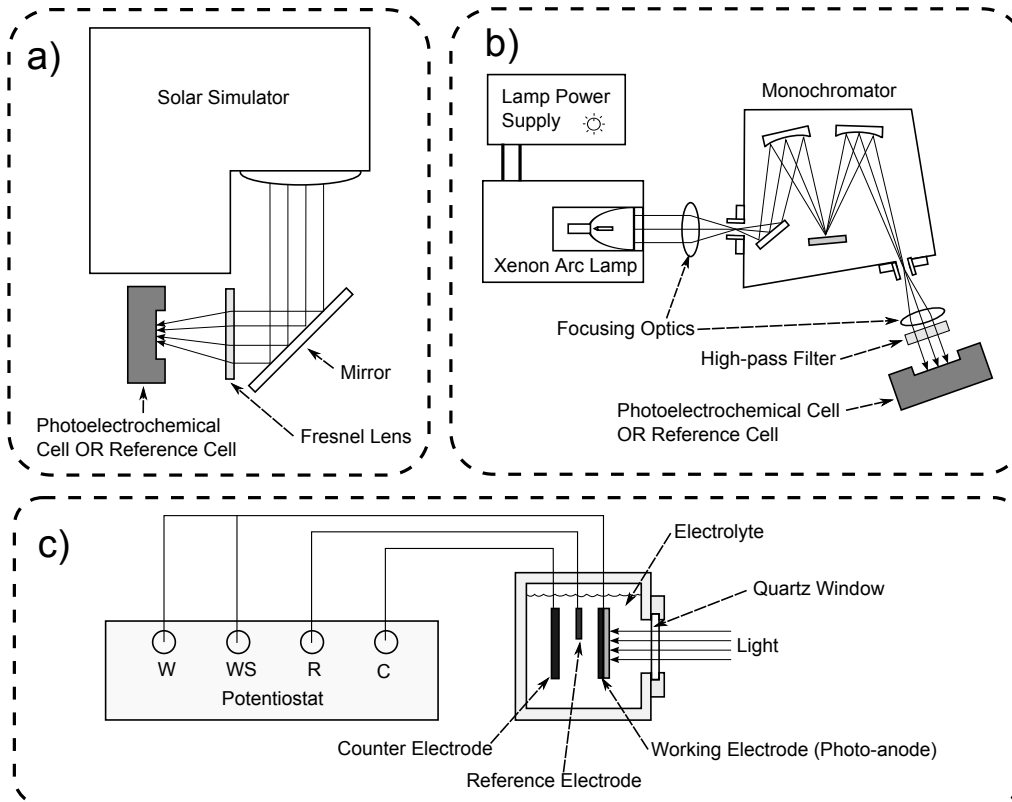


Figure 2.3: a) Solar simulator light set up b) Xenon arc lamp and monochromator set up c) photo-electrochemical cell and potentiostat

simulated broadband solar light (*e.g.* solar simulator). The IPCE is measured through photo-current spectroscopy using monochromated light and probing the system at a number of wavelengths. The STH efficiency can be estimated from the photo-current spectroscopy by integrating the IPCE multiplied by the spectral photon flux q_p and the elementary electronic charge q over the entire light spectrum and is given in Eq. (2.14). The optical properties of the photo-electrode can be determined using UV-vis spectroscopy, and from this and the IPCE, the APCE can be calculated.

$$j_{photo} = \int_0^{\infty} (q_e \eta_{IPCE}(\lambda) q_p(\lambda)) d\lambda \quad (2.14)$$

Faradaic efficiency is assessed by measuring the amount of products produced compared to the current flowing, often by collecting the H_2/O_2 gas and measuring the volumetric rate of production. Other analytical methods can be used to determine gas production rates such as gas chromatography/mass spectrometry and dissolved gas concentration can be assessed *via* electrochemical detection such as amperometric detection of oxygen with a Clark electrode.

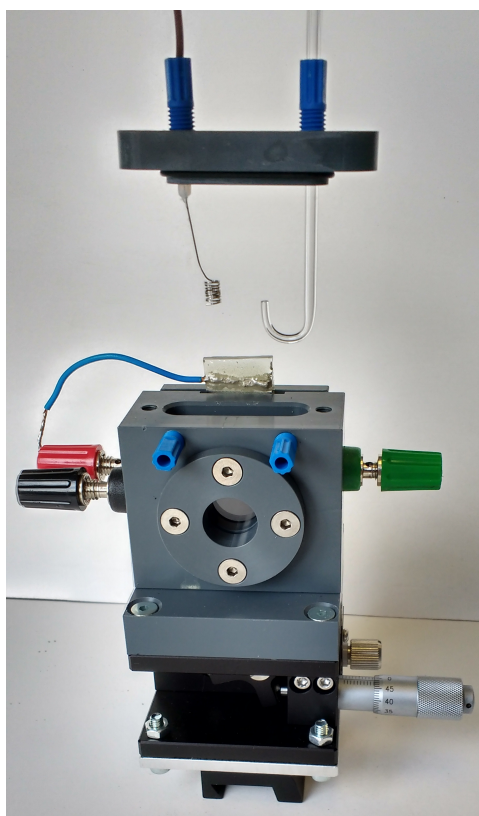


Figure 2.4: Example of self designed PEC cell

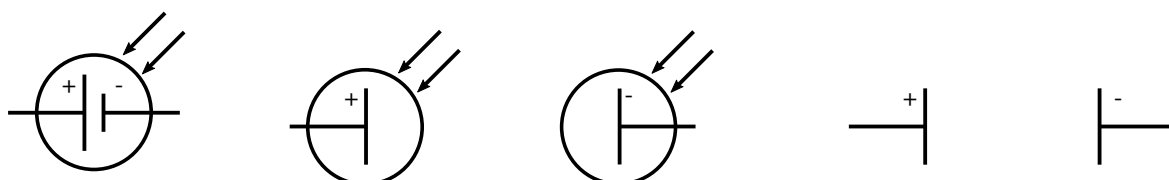
Chapter 3

Efficiency of photo-electrochemical water splitting

Understanding the fundamental thermodynamic limits of photo-electrochemical water splitting is important from both a scientific and a practical perspective. Therefore, a PEC device configuration framework is introduced, alongside an open source tool for calculating the limiting efficiencies. This is used to investigate strategies which may realise high efficiencies and appraise the realised potential of experimental designs from selected literature.

This chapter is partially based on the author's publications:

[3] I. Holmes-Gentle, K. Hellgardt, "A Versatile Open-Source Analysis of the Limiting Efficiency of Photo Electrochemical Water-Splitting", *Scientific Reports* **2018**, 8, DOI 10.1038/s41598-018-30959-9



3.1 Introduction

The fundamental efficiency limits of quantum energy converters have been studied in great detail since the seminal work of Shockley and Queisser [62], who laid the foundations of the *detailed balance* or *Shockley-Queisser limit* often discussed today. Similarly, this detailed balance theory can be applied to photo-electrochemical energy conversion where the seminal works are critically reviewed in a book chapter by Bolton *et al.* [63]. Notably, they demonstrated the equivalence of many of the historical models. In more contemporary work, researchers have focused on the practical efficiency limits of PEC water splitting [64–71] along with different optical configurations [65, 66]. This is summarised in Table 3.1, which gives a chronological overview of some of the more important studies since Shockley and Queisser’s formative paper.

Typically, the theoretical models used to calculate the limiting efficiency are well documented but the actual process of numerical solution is often ambiguous or absent. Furthermore, any numerical code used is commonly not openly available. Work by Seger *et al.* [68] aimed to address this exact issue and provide researchers with a web based tool (www.solarfuelsmodeling.com) for calculating the limiting and realistic efficiency of tandem and single photo-absorber devices. Whilst an undeniably useful tool, the fixed configuration (optically and electrically in series) and limited number of allowable photo-absorbers (up to 2) means there is opportunity for a more versatile open source model. Consequently, the generic model and code described in the chapter was created to fill this gap.

Another reason that there is potentially a need for easily available tools to calculate photo-electrochemical efficiency, is that some researchers have calculated the STH efficiency whilst neglecting the inescapable radiative emission (see Ref. [76, Fig. 2], [77, Fig. 2], [14, Fig. 7.15 & 7.23], [66, Fig. 2a]). There are unavoidable free energy losses at feasible device and sun temperatures, which means that a solar quantum energy converter (which is a type of heat engine) cannot outperform the fundamental Carnot efficiency limit for heat engines [63, 78]. The difference between a ‘1st law’ type analysis, which assumes that 100% of the energy that can be captured (above bandgap photons) is converted to useful work, and a ‘2nd law’ or detailed balance type analysis, which includes the intrinsic free energy losses, can be seen in Figure 3.1. Whilst the simplistic 1st law analysis for a single photo-absorber system appears accurate for higher bandgaps (>1.6 eV), it fails to capture the limiting efficiency of lower bandgap materials. It is, therefore, arguably important to use efficiency limits that are thermodynamically possible (even if they are realistically impossible), when discussing the fundamental limits of water splitting.

Table 3.1: Key studies on the theoretical efficiencies of solar fuel conversion

Year	Reference	Notes
1961	Shockley and Queisser [62]	Introduced the ‘detail balance’ efficiency limit for photo-voltaic energy conversion
1977	Ross and Hsiao [72]	Generalised the efficiency limit in the context of photochemical solar energy conversion
1981	Bolton <i>et al.</i> [63]	A comprehensive review of the historical thermodynamic models with a demonstration of the equivalence of some and the inaccuracy of one
1984	Weber and Dignam [73]	Studies the effect of optical configuration on the efficiency of tandem PEC devices (side-by-side and in series configuration)
1985	Bolton <i>et al.</i> [74]	Proposes a classification system for PEC devices (<i>e.g</i> S2, D4 <i>etc.</i>) and outlines limiting and realisable efficiencies for each
2006	Hanna and Nozik [75]	Considered the limiting efficiency of absorber capable of carrier multiplication
2013	Hu <i>et al.</i> [64]	Outlined realisable efficiencies for tandem PEC devices
2014	Seitz <i>et al.</i> [65]	Investigates practical efficiencies of single and tandem PEC devices in different optical configurations (including side-by-side)
2015	Jacobsson <i>et al.</i> [66]	Examines side-by-side optical configuration for up to 4 photo-absorbers (though not a true ‘detailed balance’ type model)
2016	Fontaine <i>et al.</i> [67]	Comprehensive analysis of the thermodynamic limits and realisable efficiency for two typical PEC devices
2017	Seger <i>et al.</i> [68]	Released a web-based javascript code to calculate limiting and realistic efficiencies for a fixed configuration: tandem or single photo-absorber PEC that is electrically and optically in series
2018	Holmes-Gentle and Hellgardt [3]	Outlined the generalised theory for calculating the limiting efficiency of any configuration of PEC devices and released accompanying open source code

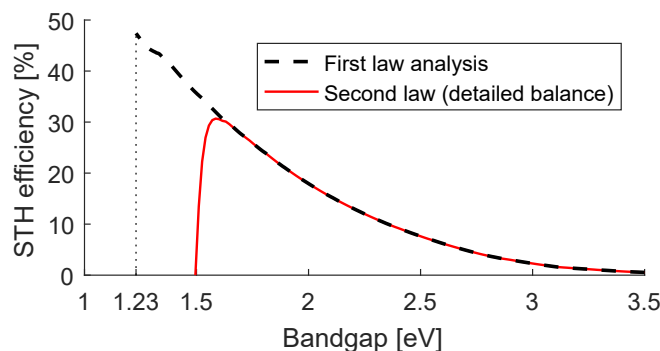


Figure 3.1: The limiting efficiencies for a single photo-absorber system (*e.g.* a one photo-electrode device)

3.2 Conceptual design of photo-electrochemical systems

The theoretical limiting efficiency of photo-electrochemical conceptual configurations can be classified by three distinct properties:

1. Number of photo-absorbers
2. Electrical configuration
3. Optical configuration

At this stage of analysis, which aims to fundamentally categorise PEC systems by the limiting efficiency, the physical structure and layout of the system is superfluous and will be discussed in the next chapter.

The configuration involves the assembly of a PEC system from its constituent components. Figure 3.2 displays these generic ‘building blocks’. Here, the self contained photo-absorber is any type of solar cell, and could range from photo-voltaics cells based on solid-state electronic junctions (*e.g.* silicon solar cells) to regenerative photo-electrochemical cells based on an electronic-ionic junctions (*e.g.* dye-sensitized solar cells). Components b) to e) are all semiconductor-electrolyte or metal-electrolyte junctions at which a reaction occurs to generate the chemical product(s) of the PEC system. At the anode, an oxidation reaction occurs and at the cathode a reduction reaction occurs, and in order for any continual current to flow a complete cell must have both electrodes so that the electrons lost from reactants by oxidation are transferred to the species that is then reduced. Therefore, both reactions are electronically balanced. This electrochemical process can occur in the light (*i.e.* components b) and c)) or dark (*i.e.* components f) and e)). In the light, this electrode is termed a photo-electrode and will be a semiconductor-electrolyte junction, whereas in the dark the electrode will commonly be a metal-electrolyte junction.

For example, in a water splitting cell there will be an anode liberating O_2 and a cathode liberating H_2 from H_2O . As this is the overall reaction that is the focus of this thesis,

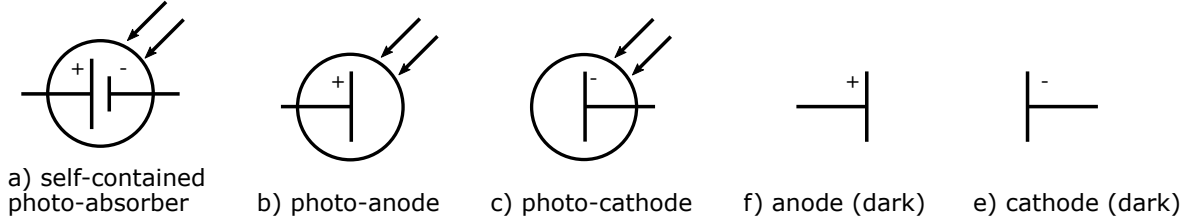


Figure 3.2: Photo-electrochemical cell components

the following analysis will specific to water splitting but this conceptual abstraction of the PEC cell may be useful for any photo-electrochemical system. The classification system presented here, is similar to efforts to create a unified taxonomy by Nielander *et al.* [79]. Their naming structure is especially useful in its objective to simplify and structure the multitude of nomenclature used to describe photo-electrochemical systems. However, as the aim of this analysis is to compute theoretical limiting efficiencies, more information about the conceptual structure is required.

3.2.1 Electrical configuration

All the constituent components in a photo-electrochemical system (*i.e.* any number and combination of components in Figure 3.2) must be electrically connected into a circuit. At a minimum, a complete photo-electrochemical cell will contain one light absorber, one anode interface and one cathode interface.

A common strategy in order to match the energy extracted from the solar spectrum to the voltage required to drive water splitting is to place multiple photo-absorbers electrically in series. In fact, recent record solar-to-hydrogen efficiencies have all employed this strategy [49, 80].

It transpires that the limiting efficiency is not impacted by whether the electrode is a combination of a self contained photo-absorber and electrode or a integrated photo-electrode [64]. Therefore, a simplifying convention for the electrical circuit diagram is made which reduces complexity of the diagram to the photo-absorbers only. For example, $\circ - (1) - (2) - (3) - \circ$ denotes three photo-absorbers in series and the circuit is completed by any number of electrolyzers in series (N_{elec}).

3.2.2 Optical configuration

The limiting efficiency of the conceptual design is inextricably connected with the optical structure of the PEC system [65]. The number of photo-absorbers N_{photo} , will be the quantity of light absorbing components (*i.e.* a) to c) in Figure 3.2). For any system with more than one photo-absorber, there will be multiple optical configurations

possible as shown in Figure 3.3. If two photo-absorbers are ‘*optically in series*’, light that is not absorbed by the first photo-absorber may pass through to be used by other photo-absorbers placed behind. Alternatively, if two photo-absorbers are placed side by side they are referred to as being ‘*optically in parallel*’.

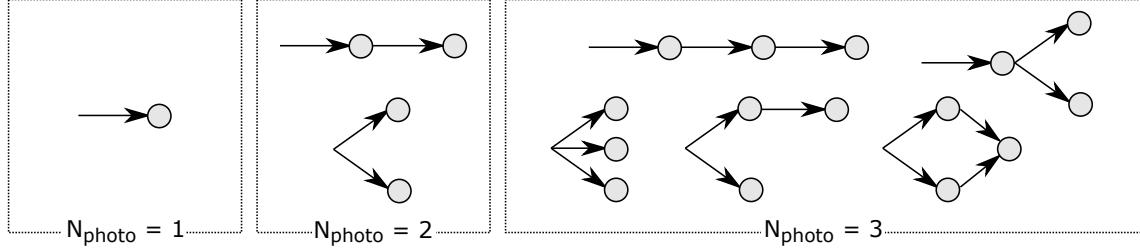


Figure 3.3: Unique optical configurations for up to three photoabsorbers

The optical configuration was represented by a directed graph schematic where the edges indicate the path of the light and all nodes after the first represent each numbered photo-electrode/photo-voltaic. The first node represents the incoming solar spectrum. For example, for a simple one photo-absorber system: $\rightarrow 1$.

The optical configuration diagram is simplified by assuming that any split in the light (*i.e.* any node which has 2+ successor nodes), is split with no spectrum splitting. Furthermore, the fractions written as the edge weight on the optical diagram are both the fractional split in the photon flux and the relative area of the subsequent node. That is, for two photo-absorbers optically in parallel: $\xrightarrow[2/3]{1/3} \frac{1}{2}$, 1/3 of the light is transferred to photo-absorber 1 which has an area is a 1/3 of the previous node and 2/3 of the light is transferred to photo-absorber 2 which has an area which is a 2/3 of the previous node.

For systems that are optically in series: $\rightarrow 1 \rightarrow 2$, light that does not get absorbed by photo-absorber 1 passes through onto photo-absorber 2. Another simplification employed is that each photo-absorber has both: 1) an abrupt absorption threshold and 2) completely absorbs above bandgap light. The simplification to the optical model reduces unnecessary complexity in the subsequent analysis and it would be straightforward to extend this to include optical losses and spectrum specific optics such as dichroic mirrors.

3.2.3 Example configurations

Following this classification system, examples of PEC cells from literature can be reduced into their respective conceptual design. Table 3.2 shows this, for various examples of water splitting, demonstrating the variety of cell types, all of which have an individual theoretical limiting efficiency according to a ‘detailed balance’ type

analysis. The power of this analysis is the ability to calculate the theoretical efficiencies of a multitude of configurations including the unconventional system proposed by Kim *et al.* [81] where 2 photo-anodes are placed electrically in parallel and optically in series. A recent study by Niu *et al.* employed a similar approach but for dual photo-cathodes [82].

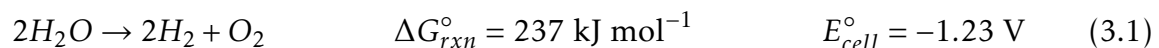
Table 3.2: Example conceptual configurations of various PEC devices

N_{photo}	Electrical	Optical	Equivalent electrical	N_{elec}	Reference
3		$\rightarrow 1 \rightarrow 2 \rightarrow 3$		1	[83]
2		$\rightarrow 2 \rightarrow 1$		1	[84]
3		$\rightarrow 1 \rightarrow 2 \rightarrow 3$		2	[49]
3		$\begin{matrix} \nearrow 1/3 \rightarrow 1 \\ \rightarrow 1/3 \rightarrow 2 \\ \searrow 1/3 \rightarrow 3 \end{matrix}$		1	[85]
2		$\rightarrow 1 \rightarrow 2$		1	[81]

3.3 Fundamental theory and calculation of limiting efficiency of solar fuel process

3.3.1 Thermodynamics of electrolysis

Equation (3.1) gives the overall chemical equation for water splitting. The minimum energy under standard conditions and at constant temperature and pressure required to drive the spontaneous splitting of water molecules is given by the standard Gibbs energy ΔG_{rxn}° . This can be subsequently expressed as a standard cell potential E_{cell}° by the relation: $\Delta G_{rxn}^\circ = -n_e F E_{cell}^\circ$ where n_e is the number of electrons transferred per product formed and F is the Faraday constant.



For an adiabatic thermodynamic system, which is defined as one where no heat transfer or mass transfer occurs between the system and surroundings, the total enthalpy of reaction $\Delta H_{rxn}^{\circ} = 286 \text{ kJ mol}^{-1}$ must be provided as electrical energy. Hence, for an isothermal system under these adiabatic conditions, this enthalpy corresponds to a cell potential of -1.48 V, namely the *thermo-neutral cell potential*.

For a isothermal system which is non-adiabatic, heat can be supplied reversibly from the surroundings at the ambient temperature (room temp. = 298.15 K). This means that a portion of the enthalpy requirement can be fulfilled by this heat, up to a thermodynamic maximum ($= \Delta H_{rxn} - \Delta G_{rxn}$). Therefore, under isothermal conditions, the minimum cell potential required will be -1.23 V. This value is used henceforth, assuming that the ambient surrounding can provide heat at 298.15 K without temperature change. For convenience, the negative sign of the cell potential will be dropped in subsequent calculations: $E_{rxn} = -E_{cell} = 1.23 \text{ V}$.

3.3.2 Efficiency of solar driven photolysis

A positive Gibbs energy and therefore a negative cell potential indicates that the chemical reaction is not thermodynamically spontaneous. Therefore, free energy is required to drive the reaction, and this can be provided by a solar energy quantum converter such as at the photo-electrochemical interface. Here, the excitation of charge carriers through absorption of solar photons and the subsequent spatial separation of holes and electrons leads to a free energy difference which can be used to drive the water splitting reaction.

PEC system are commonly categorised by the number of photo-absorbers N_{photo} , and when $N_{photo} = 2$ the system is commonly referred to as a 'tandem photo-electrochemical cell' [86]. Similarly, a PEC system can be categorised by the number of electrolytic cells N_{elec} and henceforth the analysis will investigate only electrolytic cells in series. This is as identical electrolytic cells in parallel are theoretically equivalent to a single electrolytic cell, in terms of the total thermodynamic minimum potential.

The generalised solar to fuel efficiency is defined in Equation (3.2) which corresponds to the summation of each electrolytic cell's production rate divided by the total solar power per unit area illuminated I_{solar} . Here, i is the specific electrolytic cell and N_{elec} is the total number of electrolyzers. The faradaic efficiency is given by η_f where it is the fraction of the charge used to drive the desired fuel-producing reaction. j is the current per unit area incoming light of the particular photo-electrochemical cell, which in most cases is the current density (*i.e.* current per electrode area). This cell is driven by a potential difference V , which is given by $V = E_{rxn} + V_o$ where E_{rxn} is the minimum thermodynamic potential required (as opposed to the thermoneutral) and V_o

is the overpotential required to meet the energy lost to entropy in transport and kinetic processes. In an ideal cell, the overpotential will be equal to zero.

$$\eta_{STF} = \sum_{i=1}^{N_{elec}} \frac{j_i(V_i)E_{rxn,i}}{I_{solar}} \quad \text{and therefore for } N_{photo} = 1, \quad \eta_{STF} = \frac{\eta_f j(V)E_{rxn}}{I_{solar}} \quad (3.2)$$

If the PEC device is driving multiple identical electrolytic cells that are electrically in series, then the total voltage required to drive electrolysis will be $V_{total} = N_{elec}(E_{rxn} + V_o)$. Therefore, Eq. (3.2) can be simplified to become Eq. (3.3).

$$\eta_{STF} = \frac{\eta_f N_{elec} j(V_{total}) E_{rxn}}{I_{solar}} \quad (3.3)$$

For a water splitting process, $E_{rxn} = 1.229$ [V] under standard conditions and if one assumes a faradaic efficiency of unity, the solar to fuel efficiency (STH) for a device with multiple electrolytic cells in series is expressed as Eq. (3.4).

$$\eta_{STH} = \frac{N_{elec} j(V_{total}) E_{H_2}}{I_{solar}} \quad (3.4)$$

It is important to note that the efficiency of a directly coupled PV + electrolyser or integrated PEC device is not $\eta_{STH} = \eta_{PV}\eta_{EC}$ but should include the coupling losses $\eta_{coupling}$ and any faradaic losses η_f . This is as the standalone efficiency of the solar cell(s) η_{PV} is often given at maximum power point (*i.e.* the point which satisfies $d(P_{PV})/dV = 0$) rather than at the operational potential required by the electrolysers. Therefore, as discussed by Nakamura *et al.* [80] the overall equation can be expressed as a number of elementary efficiencies: $\eta_{STH} = \eta_{PV}\eta_{coupling}\eta_{EC}\eta_f$. The coupling loss $\eta_{coupling}$ can be back-calculated from the subsequent analysis from the detailed balance thermodynamically reversible model which gives η_{STH} , assuming $\eta_{EC} = \eta_f = 1$ as there are no overpotential losses and only the water splitting reaction occurs in an ideal electrochemical cell. A decoupled system, which employs DC–DC converters, would allow the operation of the PV at the maximum power point whilst simultaneously maintaining the required potential difference for electrolysis. Whilst out of the scope of this analysis, it is important to note that there will be energy losses in the voltage conversion which would lead to an efficiency definition of the form: $\eta_{STH} = \eta_{PV}\eta_{conversion}\eta_{EC}\eta_f$.

3.3.3 Current voltage relationship of a single photoabsorber

As described by Bolton *et al.* [63], there are many equivalent approaches to determining the limiting efficiency of a solar energy to fuel process. Here a ‘detailed balance’ type

analysis is employed which was first described in the seminal work by Shockley and Queisser [62] and has been significantly extended since to a comprehensive range of scenarios. The theoretical current-voltage behaviour of an ideal solar cell is derived in this section closely following references [75, 78, 87].

The net current density is given in Eq. (3.5) by a continuity equation for the conservation of charge, namely a *detailed balance* of the current generated from the absorption of photons and the current lost due to the radiative recombination. This assumes that photons are absorbed from the surroundings and the sun, which are radiating as a blackbody at ambient and solar surface temperatures respectively. The solar cell radiates some light due to unavoidable radiative recombination and this essentially ensures that no solar energy converter could exceed the Carnot efficiency limit of any heat engine ($\eta_{carnot} = 1 - T_a/T_s$). As mentioned in the introduction to this chapter, any analysis that erroneously omits this radiative recombination will therefore be unequivocally inaccurate as explained by Bolton *et al.* [63].

$$j = j_{abs} - j_{rad} \quad (3.5)$$

The photon emissive flux normal to the surface per energy interval dE for an ideal blackbody is given by the generalised Planck's radiation law in Eq. (3.6). This includes the effect of the chemical potential $\Delta\mu$ generated from the excitation separation on the radiated photon flux [87]. In Eq. (3.6), the notation b_i denotes the photon emissive flux from a given blackbody (i) where this can be the sun (s), solar cell (e) or ambient surroundings (a). F_i is the geometric factor and is equal to π for hemispherical acceptance or emission, h is Planck constant, c is the speed of light, k is Boltzmann constant, T is the blackbody temperature T . In an ideal solar cell $\Delta\mu = qV$ as the charge transport is considered lossless [88] and for the sun and ambient surrounding, $\Delta\mu = 0$.

$$b_i(E, \Delta\mu, T) = \frac{2F_i}{h^3 c^2} \frac{E^2}{e^{(E-\Delta\mu)/kT} - 1} \quad (3.6)$$

If the ambient surrounding and the solar cell is in thermal equilibrium and there is no multiple carrier generation (*i.e.* 1 photon = 1 excited electron), then the current generated from photon absorption is given in Eq. (3.7). Here, $b_s(E)$ and $b_a(E)$ is the solar photon flux and ambient photon flux respectively, normal to the surface per energy interval dE .

$$j_{abs} = q \int_0^\infty \eta_{IPCE}(E) b_s(E, 0, T_s) + \eta_{IPCE}(E) \left(1 - \frac{F_s}{F_e}\right) b_a(E, 0, T_a) dE \quad (3.7)$$

Equation (3.7) can be further simplified if one assumes that the semiconductor has an abrupt absorption threshold and that all the excited charge carriers from the absorption

of above bandgap photons that survive radiative recombination are collected ($\eta_{IPCE} = 1$). Furthermore, if the solid angle of the sun is small in comparison to the ambient $F_s/F_e \approx 0$ and at thermal equilibrium in the dark, $b_a(E, 0, T_a) = b_e(E, 0, T_a)$. Given these assumptions, Eq. (3.7) can be expressed as Eq. (3.8).

$$\text{if } \eta_{IPCE} = \begin{cases} 1, & E \geq E_g \\ 0, & E < E_g \end{cases} \quad \text{then } j_{abs} = q \int_{E_g}^{\infty} b_s(E, 0, T_s) - b_a(E, 0, T_a) dE \quad (3.8)$$

The current lost due to unavoidable radiative recombination under illumination can be written as Eq. (3.9), by assuming the semiconductor is a selective blackbody (*i.e.* radiates photons with energy greater or equal to bandgap). For an ideal illuminated solar cell $\Delta\mu = q_e V$, given the assumptions previously discussed:

$$j_{rad} = q_e \int_{E_g}^{\infty} b_e(E, q_e V, T_a) dE \quad (3.9)$$

By substituting Eq. (3.8) and Eq. (3.9) into Eq. (3.5), the net current density can be expressed as Eq. (3.10).

$$j = q_e \int_{E_g}^{\infty} b_s(E, 0, T_s) - (b_e(E, q_e V, T_a) - b_e(E, 0, T_a)) dE \quad (3.10)$$

For large enough bandgaps (> 0.2 eV), the radiative recombination of the solar cell under illumination can be approximated by Eq. (3.11) [89, 90].

$$b_e(E, q_e V, T_a) = \frac{2f_g\pi}{h^3c^2} \frac{E^2}{e^{(E-q_eV)/kT_a} - 1} \approx \frac{2f_g\pi}{h^3c^2} \left(e^{q_eV/kT_a} \frac{E^2}{e^{E/kT_a} - 1} \right) \quad (3.11)$$

Equation (3.11) also introduces a geometric factor f_g for radiative emission from a planar solar cell, which is equal to 2 when the cell can radiate from both sides and 1 when the radiative emission is constrained to the front side only. Hemispherical emission $f_g = 1$ can be achieved with perfect rear reflector however this approach cannot be used for a solar cell which must pass sub-bandgap light though onto another solar cell below (*i.e.* optically stacked).

Following this derivation, we therefore can approximate the ideal current voltage relationship of the solar cell with the *ideal diode equation* given in Eq. (3.12) where j_o is commonly called the *dark saturation current*.

$$j = j_L - j_o(e^{(kV/kT_a)} - 1) \quad \text{where } j_o = \frac{2f_gq_e\pi}{h^3c^2} \int_{E_g}^{\infty} \frac{E^2}{e^{E/kT_a} - 1} dE \quad (3.12)$$

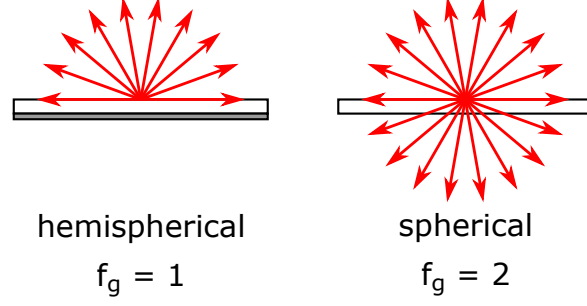


Figure 3.4: Radiative emission from a planar cell with various geometric factors f_g

From the derivation, j_L therefore must be equal to $q \int_{E_g}^{\infty} b_s(E, 0, T_s) dE$ which is the amount of current generated from solar photons. This can be calculated in two ways. Firstly, the sun can be approximated as a black body at a temperature of ~ 6000 K, in which case $j_L = q \int_{E_g}^{\infty} b_s(E, 0, 6000K) dE$ where b_s is calculated using Planck's law (Eq. (3.6)). Secondly, j_L could be calculated using dataset representative of the terrestrial solar spectrum, such as the standardised ASTM G173-03 reference spectra for hemispherical light on a 37° tilted surface with an air mass coefficient of 1.5 (AM1.5G) [55]. Consequently, j_L would be evaluated *via* Eq. (3.13).

$$j_L = q_e \int_{E_g}^{\infty} b_{AM1.5G} dE \quad (3.13)$$

3.3.4 Optical configuration

The optical configuration was represented as a directed acyclic graph. Graph theory is a mathematical abstraction where objects are represented by nodes and the relationship between objects represented by edges. For directed graphs, each edge has a directionality and the directed graph is acyclic if there are no directed cycles, that is to say no closed loops.

The input light spectrum (*e.g.* AM1.5G) is represented by the first node and photo-absorbers are placed at each subsequent node. The nodes are connected together by edges which represent the path of the light. The directed acyclic graph for various example optical configurations can be seen in Fig. 3.3 and in Fig. 3.5 b).

Figure 3.5 a), displays the notation using an example optical configuration. The light entering and leaving the photoabsorber at node i is denoted as b_i^- and b_i^+ respectively and therefore light at the input node (node 0) will be $b_0^+ = b_{AM1.5G}$.

For an edge that connects node i to j , the split fraction f_{ij} and the area concentration c_{ij} is defined by Eq. (3.14). The split fraction denotes the fraction of light arriving at node j from node i , to the total amount of light leaving node i . The area concentration is the

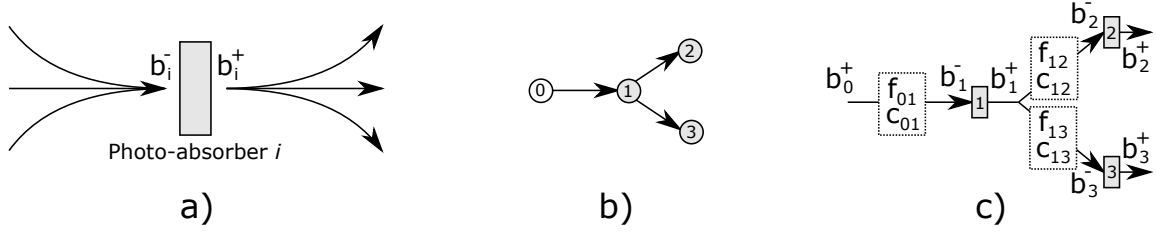


Figure 3.5: a) Diagram of notation for photoabsorber node i , b) an example optical configuration showing the directed graph c) the same configuration showing the notation for nodes and edges

ratio of the photo-absorber area of the subsequent node j to the previous node i . These two properties of the edge lead to a more generic treatment of the optical configuration where f_{ij} does not necessarily equal c_{ij} . Here b_{ij} is the photon flux from node i to node j .

$$f_{ij} = \frac{b_{ij}A_j}{b_i^+A_i} \quad c_{ij} = \frac{A_j}{A_i} \quad (3.14)$$

As the graph is acyclic, the topological order can be computed which then defines the order in which the equations are numerically evaluated. That is to say, before the light at a successor node is calculated, the light at all the predecessor nodes will be first calculated. The light that arrives at node i will be the summation of the light leaving previous nodes, taking the fraction of light and area concentration into account (Eq. (3.15)). Then, the light that passes through photo-absorber i is calculated by Eq. (3.16) where the transmittance $T_i(E)$ of photo-absorber i is assumed to be a Heaviside (unit) step function.

$$b_i^- = \sum_{\forall j} f_{ij}c_{ij}b_j^+ \quad \text{for all predecessor nodes, } j, \text{ to node } i \quad (3.15)$$

$$b_i^+ = T_i(E)b_i^- \quad \text{where} \quad T_i = \begin{cases} 0 & E \geq E_{g,i} \\ 1 & E < E_{g,i} \end{cases} \quad (3.16)$$

Finally, in order to use the ideal diode equation (Eq. (3.12)) to model each photo-absorber, the current generated by the light absorption j_L must be calculated *via* an equation analogous to Eq. (3.13). For each node i , this current can be calculated by Eq. (3.17) from the spectral irradiance falling on that photo-absorber b_i^- .

$$j_{L,i} = q_e \int_{E_{g,i}}^{\infty} b_i^- dE \quad (3.17)$$

3.3.5 Electrical configuration

After the optical configuration of the PEC system is set up, the currents and voltages of each electrical connection within the system is evaluated. In order to simplify the solution process, electrolyzers are assumed to be in series and grouped together, which are arbitrary assumptions when evaluating the theoretical limiting efficiency. Therefore, the electrical potential difference required by the electrolyser(s) will be $V_{total} = N_{elec}(E_{rxn} + V_o)$ where V_o is the overpotential of each cell. This total voltage required (V_{total}) is provided by the photo-absorber circuit.

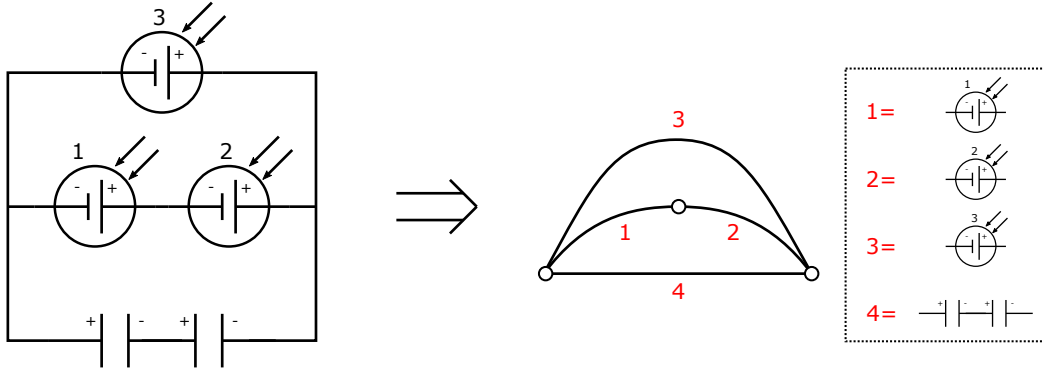


Figure 3.6: An example of an electrical configuration and its corresponding directed cyclic graph

The electrical circuit is then mathematically abstracted to become a directed cyclic graph, and an example of this process is shown in Figure 3.6. Each branch represents an individual PV component except for the final branch which represents the series connected electrolyzers grouped together. In order to represent all the permutations of design using MATLAB inbuilt functions, a third type of branch which constitutes a simple lossless electrical connection was included. This is due to the fact that the inbuilt functions in MATLAB do not permit multigraphs which are graph structures with multiple edges between nodes.

As the ideal diode equation for photo-absorbers is non-linear, non-linear circuit analysis is employed in order to calculate the current and voltages of each branch. The methodology used is the 'tableau matrix' analysis as described by Chua, Desoer and Kuh [91] in their book: *Linear and Nonlinear circuits*. This is outlined in detail in Appendix 11.1, along with the choice of scaling and initial guesses for the iterative non-linear root finding method used.

3.4 Open source software

The calculation of photo-electrochemical device limiting efficiency was conducted in MATLAB and the resulting code named ‘etaPEC’ made open source. A graphical user interface was constructed and an example screen-shot can be found in Figure 3.7. The software was released under the GNU General Public License v3.0 which allows researchers to modify and adapt the script to meet their needs with the correct attribution. The software can be found at: <https://github.com/IsaacGentle/etaPEC>

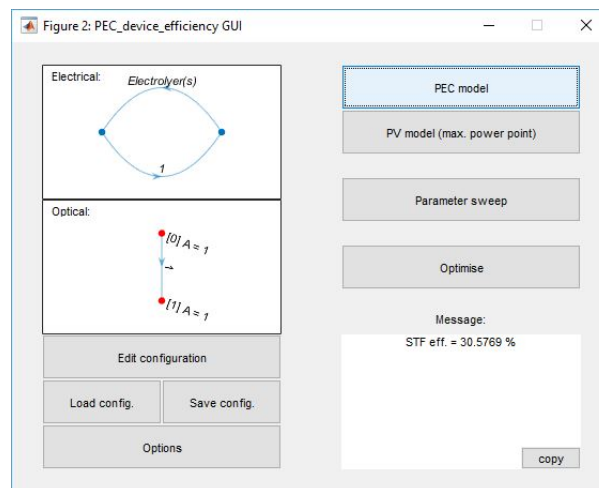


Figure 3.7: Screen-shot of etaPEC graphical user interface

The rationale for releasing the code as open source, was two-fold: 1) to facilitate the scrutiny of the code for integrity 2) to give the research community a tool to easily calculate limiting efficiencies of complicated PEC configurations using a rigorous ‘detailed balance’ approach.

Greater detail on the inner workings of the code can be found in the wiki page hosted on GitHub and only an overview is given here for clarity. An overview of the inputs and outputs of the code is found in Figure 3.8 and a flowchart of the numerical algorithm is shown in Figure 3.9.

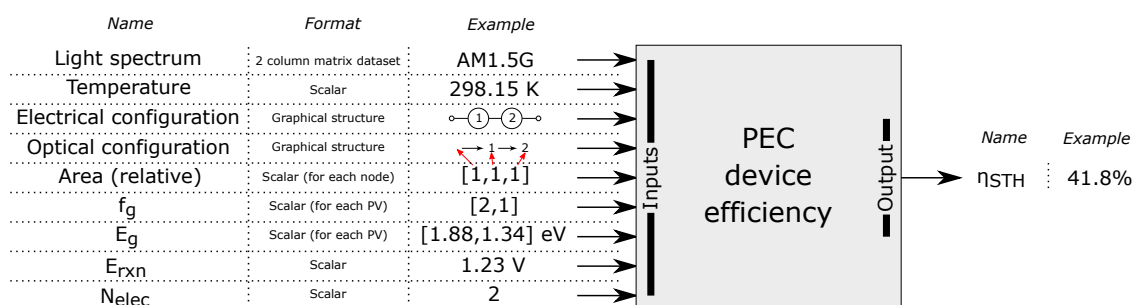


Figure 3.8: Schematic of model inputs and outputs with example data

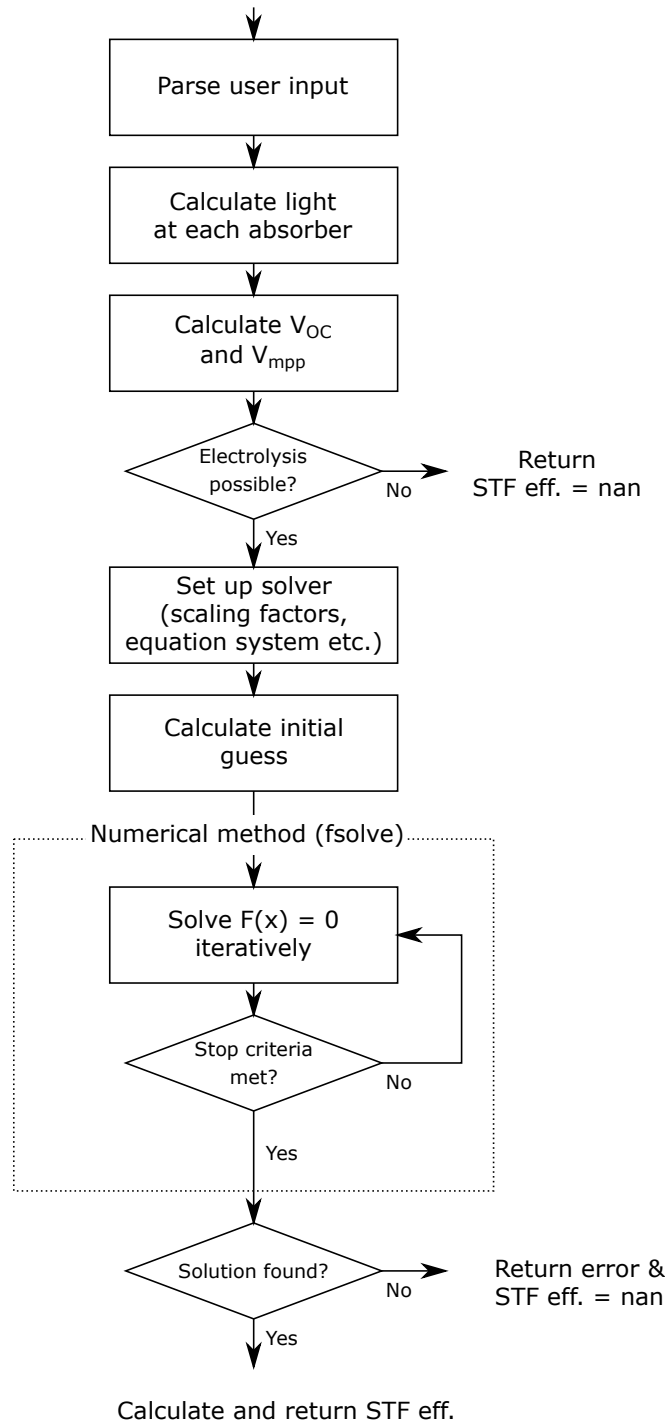


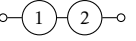
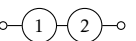
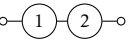
Figure 3.9: Numerical algorithm flowchart of the etaPEC code

3.4.1 Validation of code against literature

The etaPEC code was validated against previous results from literature and an overview of this comparison is given in Table 3.3. Comparison was made only with ‘detailed balance’ type models and the calculated efficiencies were found to be very similar. Effort was made to ensure that all input parameters to the model were identical to the comparative literature. Therefore, when evaluating the efficiency to compare with Bolton *et al.* [74], a historical standard of solar spectrum was used [92] in contrast with the contemporary standard: ASTM G173 [55]. In spite of this, a slight difference in results was established which could perhaps be due to a different numerical methods used as Bolton *et al.* [74] do not go into the details of the solution process. Secondly, discrepancies were noted in Bolton’s paper for the tandem cell configuration (named ‘D4’ in the paper) where a second threshold wavelength (2,610 nm) was suggested that was larger than the largest value in the spectral irradiance data given by Bird *et al.* [92] (2,450 nm) and this indicates that we have not completely replicated their numerical method. That being said, the differences are minor and so the code is validated.

The model was not compared to results from Hu *et al.* [64] or Seitz *et al.* [65] as both studies were modelling practical limits of photo-electrochemical water splitting as compared to fundamental thermodynamic limits, and so included losses which are not thermodynamically intrinsic (*e.g.* overpotentials, recombination *via* non-radiative pathways *etc.*). In addition to this, whilst our results are similar, direct comparison with work by Jacobsson *et al.* [66] could not be made as they assumed a fixed energy loss due to charge carrier separation of 0.4 eV rather than one calculated from the ‘detailed balance’.

Table 3.3: Validation of the model by comparison with existing literature

Ref	Electrical	Optical	Potential	Reported η_{STH}	This work η_{STH}	Notes
[75, 93]		$\rightarrow 1$	mpp	33.7 (1.34 eV)	33.7 (1.34 eV)	AM1.5G, T = 300 K, $f_g = 1$
[74]		$\rightarrow 1$	1.229 V	30.7(1.60 eV)	30.7(1.59 eV)	(S2), historical AM1.5G spectrum [92], T = 300 K, $f_g = 1$ assumed
[67, 75]		$\rightarrow 1$	1.23 V	30.6 (1.59 eV)	30.6 (1.59 eV)	AM1.5G T = 300K, $f_g = 1$
[74]		$\rightarrow 1 \rightarrow 2$	1.229 V	41.0(1.36, 0.48 eV)	40.4 (1.39, 0.51 eV)	(D4), historical AM1.5G spectrum [92], T = 300 K, $f_g = 1$ assumed for both
[67]		$\rightarrow 1 \rightarrow 2$	1.23 V	40.0 (1.40,0.52eV)	39.8 (1.40,0.52eV)	AM1.5G, $f_g = 2$ for top cell and $f_g = 1$ for top cell. T not given (assumed 300 K).
[75]		$\rightarrow 1 \rightarrow 2$	1.23 V	40.0 (1.40,0.52 eV)	40.0 (1.40,0.52 eV)	AM1.5G, T = 300 K and $f_g = 1$ for both cells

3.5 Theoretical limiting efficiencies of permutations of PEC design

In this section, the ability of the code to calculate the theoretical limiting efficiencies of permutations of photo-electrochemical conceptual design was leveraged in order to investigate potential strategies to high efficiency solar water splitting.

3.5.1 Single photo-absorber

For a single photo-absorber, there is only one optical and one electrical configuration. This means the whole limiting efficiency *vs.* bandgap relationship can be aggregated into one graph, *i.e.* Figure 3.10. This plot shows the distinctive PEC efficiency curve compared to the PV efficiency at maximum power point and demonstrates the maximum PEC efficiency corresponds to an exact match between the maximum power point voltage V_{mpp} and the voltage required to drive electrolysis V_{total} . At smaller bandgaps than this maximum, the system quickly becomes voltage limited and at larger bandgaps, the photo-absorber provides a greater voltage than required and accordingly the efficiency drops. For water splitting and one electrolytic cell $V_{total} = E_{rxn} = 1.229$ [V] and for two electrolytic cells in series $V_{total} = N_{elec}E_{rxn} = 2.458$ [V]. Therefore, in order to drive two electrolytic cells in series the bandgap must be significantly larger.

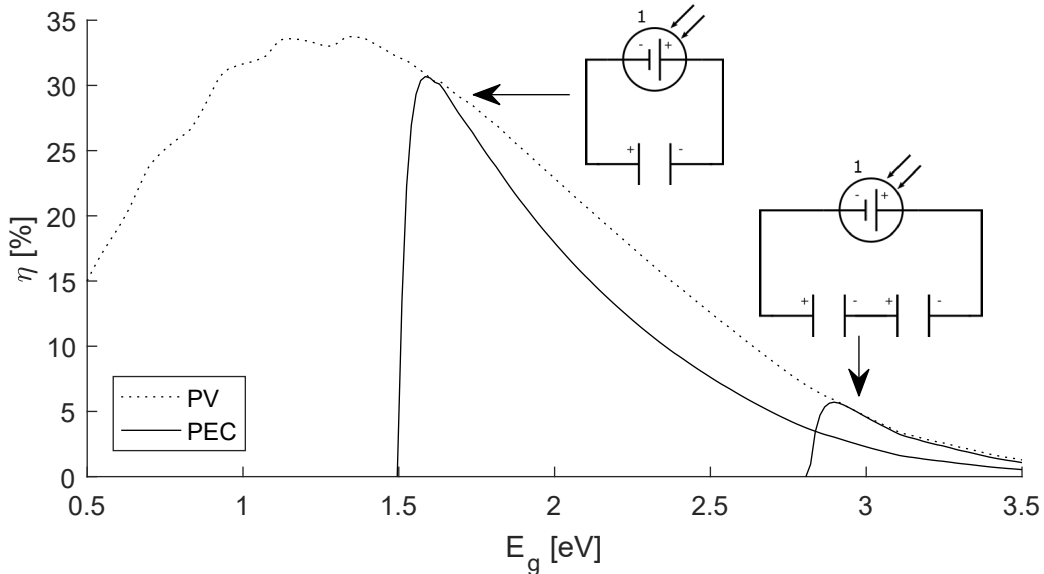
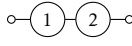
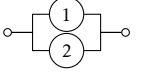
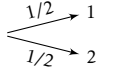


Figure 3.10: Single photo-absorber efficiency showing connection with one and two electrolyzers (solar spectrum = AM1.5G, $T = 298.15$ K)

3.5.2 Two photo-absorbers

For tandem designs, that is designs which have two photo-absorbers, there will be a number of permutations of design. As the electrical configuration of the photo-absorber system is separate to the electrolyser system in this analysis, the following arrangements of each distinct element of the system is as follows:

- Electrical configurations (photo):  
- Electrical configurations (electrolysers): $N_{elec} = 1$, $N_{elec} = 2$...
- Optical configurations: $\rightarrow 1 \rightarrow 2$ 

For tandem systems and a standard terrestrial solar spectrum, the feasible number of electrolysers in series is up to two N_{elec} . Furthermore, because a parallel photo-absorber configuration is not very successful in achieving high efficiencies it will be dropped from the analysis to further reduce the number of permutations of design. Therefore, there will be four permutations of design studied here (2 optical $\times$ 1 electrical (photo) $\times$ 2 electrical (electrolyser) = 4).

The limiting efficiency of these permutations *versus* both bandgaps ($E_{g,1}$ and $E_{g,2}$) can be seen in Figure 3.11. When the two photo-absorbers are optically in series, the second cell absorbs and utilises light which has not been captured by the first. Hence for single bandgap systems, the first cell must have a higher bandgap than the second ($E_{g,1} > E_{g,2}$). Shown in Figure 3.11, the limiting efficiency is improved significantly by operation with two photo-absorbers as compared to the case for single photo-absorber systems (Figure 3.10). For comparison, the standalone PV efficiency (at maximum power point) is given in Figure 3.12.

When the cells are optically in parallel (Fig. 3.11), the highest limiting efficiency is found when $E_{g,2} = E_{g,1}$, that is when both cells are identical. Therefore, the maximum limiting efficiency for cells optically in series can be more conveniently displayed on a 2D plot as efficiency *vs.* bandgap of all cells.

3.5.3 Global limiting efficiency for selected permutations of design

For various conceptual designs with up to 3 photo-absorbers and 3 electrolysers, there will be an optimal bandgap or bandgaps which maximise the limiting solar-to-hydrogen efficiency η_{STH} . Henceforth, this maximum efficiency is referred to as the *global limiting efficiency* of that conceptual configuration and the bandgap optimisation is expressed mathematically in Eq. (3.18).

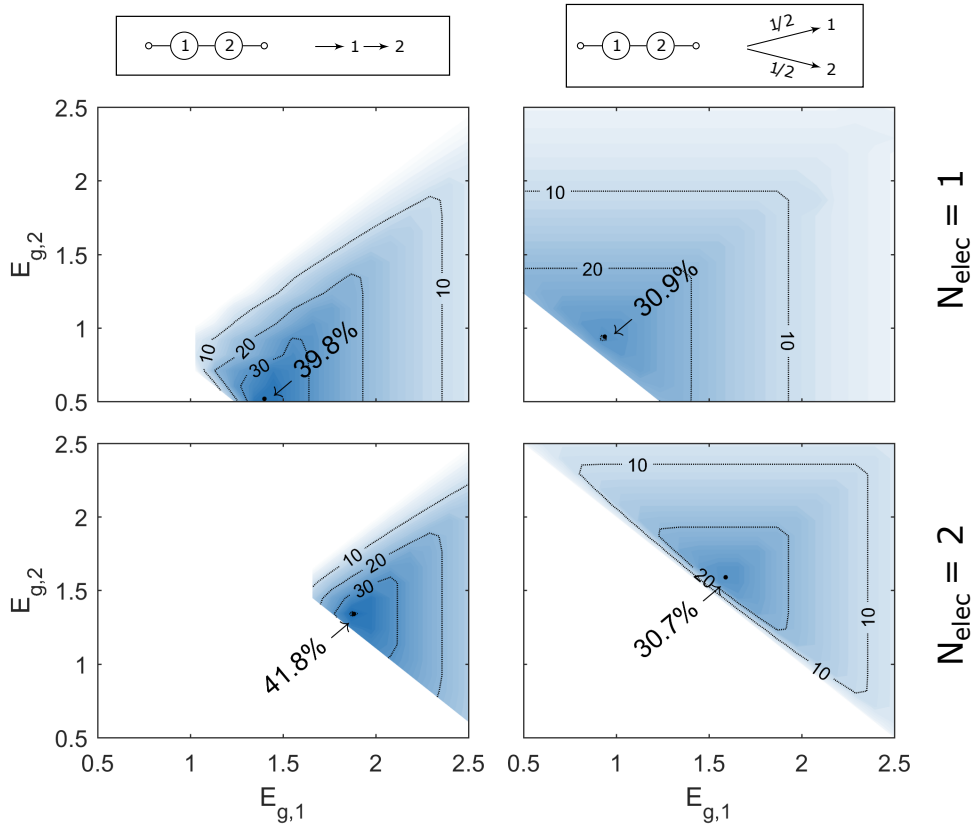


Figure 3.11: STH Efficiency of various configurations tandem cells, showing optically in series *vs.* in parallel for 1 and 2 electrolyzers N_{elec}

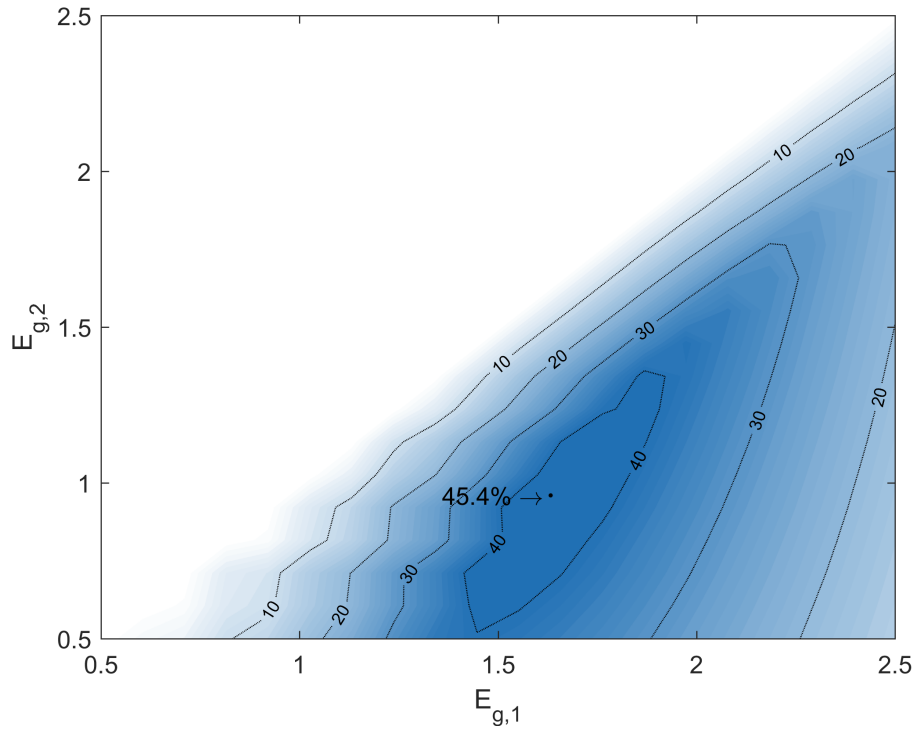
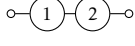
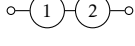
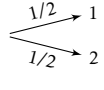
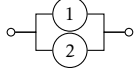
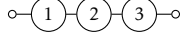
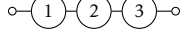
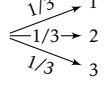
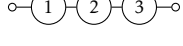
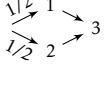
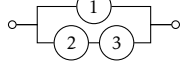


Figure 3.12: Maximum efficiency of series connected (optically and electrically) tandem photovoltaic system

Table 3.4: Limiting efficiency of selected permutations of design (AM1.5G, Sun = 1, $T = 298.15$ K)

N_{photo}	Electrical	Optical	N_{elec}	N_{elec}/N_{photo}	$\eta_{STH_{opt}}$ [%]	$E_{g,opt}$ [eV]
1		$\rightarrow 1$	1	1	30.7	1.59
			2	2	5.71	2.89
			3	3	-	-
2		$\rightarrow 1 \rightarrow 2$	1	0.5	39.8	1.40, 0.52
			2	1	41.8	1.88, 1.34
			3	1.5	23.7	2.47, 2.04
			1	0.5	30.9	0.94, 0.94
			2	1	30.7	1.59, 1.59
			3	1.5	17.5	2.24, 2.24
		$\rightarrow 1 \rightarrow 2$	1	0.5	30.7	1.96, 1.59
			2	1	5.72	2.89, 3.08
			3	1.5	-	-
		$\rightarrow 1 \rightarrow 2 \rightarrow 3$	1	0.33	25.0	1.77, 1.18, 0.67
			2	0.66	49.6	1.77, 1.19, 0.69
			3	1	47.2	2.07, 1.57, 1.19
			1	0.33	23.9	0.72, 0.72, 0.72
			2	0.66	33.6	1.15, 1.15, 1.15
			3	1	30.7	1.59, 1.59, 1.59
3		$\rightarrow 1 \begin{matrix} \nearrow 1/2 \\ \searrow 1/2 \end{matrix} \begin{matrix} 2 \\ 3 \end{matrix}$	1	0.33	27.7	1.71, 0.49, 0.49
			2	0.66	42.6	1.88, 0.92, 0.92
			3	1	41.9	2.15, 1.34, 1.34
			1	0.33	27.4	1.08, 1.08, 0.46
			2	0.66	42.2	1.35, 1.35, 0.92
			3	1	39.4	1.72, 1.72, 1.39
		$\rightarrow 1 \begin{matrix} \nearrow 1/2 \\ \searrow 1/2 \end{matrix} \begin{matrix} 2 \\ 3 \end{matrix}$	1	0.33	45.6	1.63, 0.94, 0.94
			2	0.66	33.3	2.93, 1.59, 1.59
			3	1	-	-

$$\eta_{STH,opt}(E_{g,opt}) = \max_{E_g \in \mathbb{R}} \left(\eta_{STH}(E_g) \right) \quad (3.18)$$

Table 3.4 displays the global limiting efficiency for various electrical and optical conceptual designs. This clearly demonstrates the vast array of conceptual designs which are capable of high efficiencies, and the code's capability to handle different designs which constitutes an improvement on previous open source PEC models [68]. Some of the more esoteric conceptual designs, such as the final entries in Table 3.4, have been proposed as potentially advantageous by White *et al.* [94] and Brillet *et al.* [86].

3.5.4 Strategies to improve the maximum limiting efficiency

A number of strategies have been identified in order to improve the maximum limiting efficiency of solar energy to hydrogen fuel conversion and these methodologies are outlined in the following sections.

Repeating photo-absorber units electrically in series and optically in parallel

If the photo-absorbers and the electrolyzers components of the system are not integrated and so the configuration of each can be independently adjusted, the voltage requirement of the electrolyzers can be adjusted to match the maximum power point of the photo-voltaic system and this type of optimisation has been previously discussed and demonstrated [70, 80, 94, 95]. This can be achieved by repeating photo-absorber units electrically in series and optically in parallel (equal fraction of total light for each repeating unit) connected to electrolyzers electrically in series.

An interesting property of these systems is that the limiting efficiency is only dependant on the ratio of the number of electrochemical cells (N_{elec}) to number of repeating units (N_{RU}). This can be demonstrated for the case where $N_{elec}/N_{RU} = 1$ in the equation schematic shown in Eq. (3.19), where blue lines indicate optical connections and black lines indicate electrical connections.

$$\text{[Schematic Diagram]} = \text{[Schematic Diagram]} = \text{[Schematic Diagram]} \quad (3.19)$$

As previously mentioned, this type of optimisation of matching electrical generation to load can only be achieved for systems where the configuration of the photo-absorber is not inherently connected to the number of electrolytic cells (*e.g.* PV + electrolyser). In an integrated photo-electrochemical system, this repeating unit connection ratio may be inherently constrained by the conceptual design as the electrochemical interface may be part of the repeating unit (*i.e.* N_{RU} and N_{elec} are dependent variables).

In order to demonstrate this, the simplest repeating unit ($\boxed{?}$) of a single photo absorber ($\text{---} \textcircled{1} \text{---}$, $\rightarrow 1$) will be used as an example. Then, the repeating unit connection ratio can be defined as $S = N_{elec}/N_{photo}$ as $N_{photo} = N_{RU}$ and the limiting efficiency of the system can be plotted against the bandgap of the single photo-absorber in the repeating unit, as shown in Figure 3.13. This clearly shows the PEC efficiency curve can be shifted to optimise the solar-to-hydrogen efficiency. If the value of S is fixed at unity by say a single photo-anode PEC system, the global limiting efficiency will be 30.7%. Alternatively, if the S is allowed to be optimised, a maximum of 33.8% can be achieved and is found at a value of $S = 0.801$ and $E_g = 1.34$ eV. This repeating unit connection ratio $S = 0.801$ approximately corresponds to 5 single photo-absorbers in series driving 4 electrolyzers in series. This methodology allows the PEC efficiency η_{PEC} to be optimised towards the single junction PV efficiency at maximum power point η_{PV} and in the case of no kinetic losses, η_{PEC} can equal η_{PV} exactly. Such optimisation has been previously discussed by Patel *et al.* [70] who investigated a system where the repeating unit is a monolithic multiple junction solar cell.

Effect of solar concentration

Solar concentration can improve the efficiency of the solar energy capture process [96]. Furthermore, for specific PEC systems, solar concentration can improve the maximum efficiency to a larger extent than just the improvement in PV with solar concentration. The PV and PEC efficiency (for $S = 1$) is shown in Figure 3.14, and displays this improvement with solar concentration. This can be explained by the increase in the open circuit voltage of the photo-absorbers as the solar spectrum is concentrated, which can allow the PEC to operate at smaller bandgaps whilst still providing 1.229 V per cell to drive the electrolytic decomposition of water. This may reduce the issue of matching the energy of incoming photons to the energy required to drive water splitting, termed the “solar spectrum mismatch problem” by Jacobsson *et al.* [66]. For $S = 1$, the PV efficiency is higher at smaller bandgaps and therefore, as solar irradiance (measured in multiples of the sun’s power) increases, the PEC efficiency increases significantly.

On the other hand, solar concentration increases the complexity of the engineering design and reduces the amount of diffuse light captured (due to the acceptance angle of the concentrating optics). Therefore, a full technical and economic analysis would be required to fully support the implementation of concentrated solar PEC systems, but from a purely thermodynamic view using this simple model, solar concentration can significantly improve the theoretical limiting efficiency.

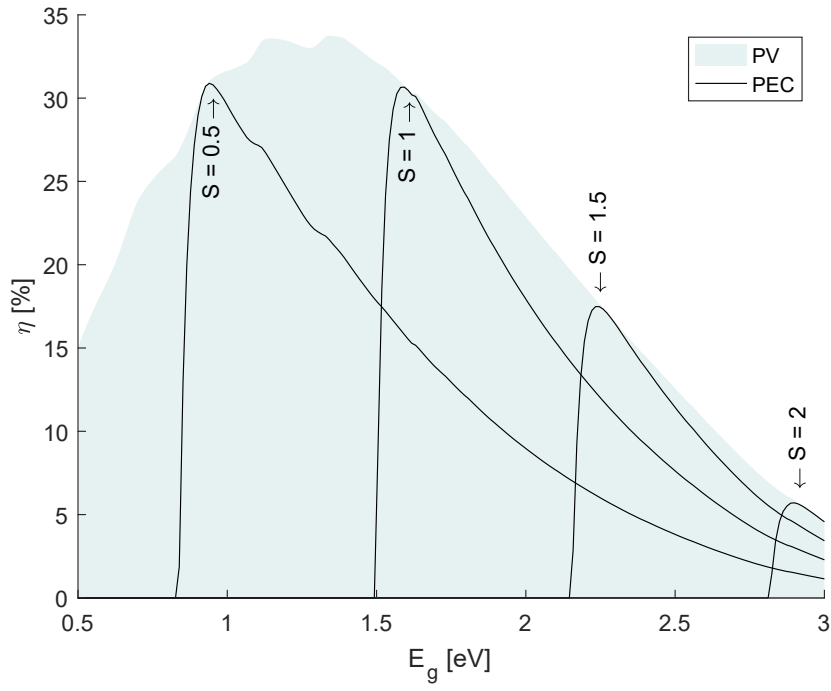


Figure 3.13: Efficiency of PV (at mpp) and PEC/PV+EC system at various repeating unit connection ratios, S

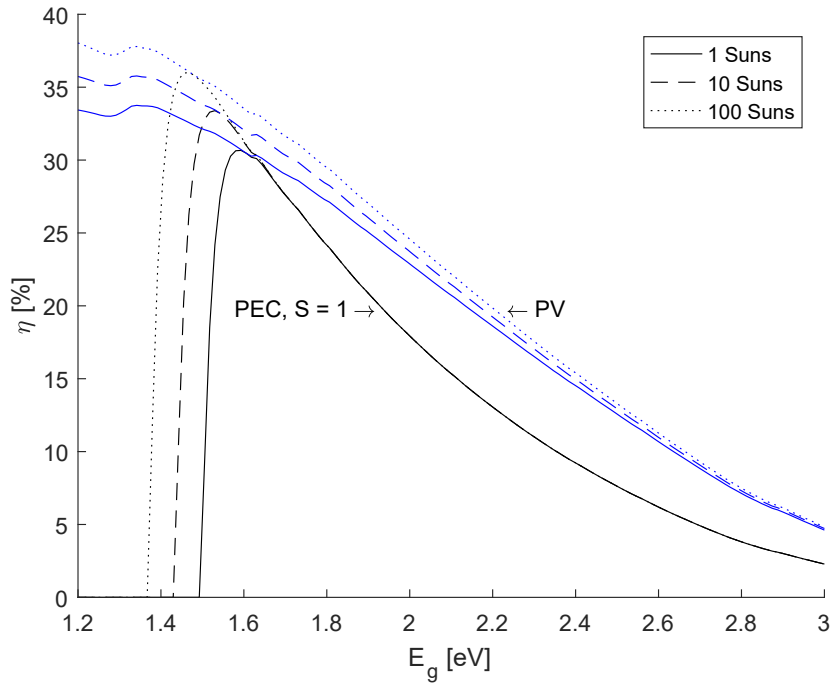


Figure 3.14: Efficiency of PEC system ($S = 1$) at various solar concentrations

Hybrid PV-thermal-electrolysis systems

The first law of thermodynamics, under steady state, can be written as Eq. (3.20) by neglecting any of the kinetic and gravitational contributions for the input and output mass. Here, the sign conventions used are that, for both heat transferred Q and work done W , the quantity is positive when it is to the system from surrounding. Under reversible conditions, the work required to drive the reaction W_{rev} is equal to the Gibbs energy of reaction ΔG_{rxn} and the heat transferred is equal to the change in entropy due to reaction ΔS_{rxn} multiplied by the temperature at which the heat was transferred T .

$$\Delta H_{rxn} = W + Q = \Delta G_{rxn} + T\Delta S_{rxn} \quad (3.20)$$

As can be seen in Figure 3.15, the reversible work required is reduced as electrolysis proceeds at elevated temperatures. As the temperature increases, the minimum thermodynamic cell potential (related to the Gibbs energy) decreases. These thermodynamic properties, ΔH_{rxn} , ΔG_{rxn} , $T\Delta S_{rxn}$, were calculated from datasets provided by NIST [97].

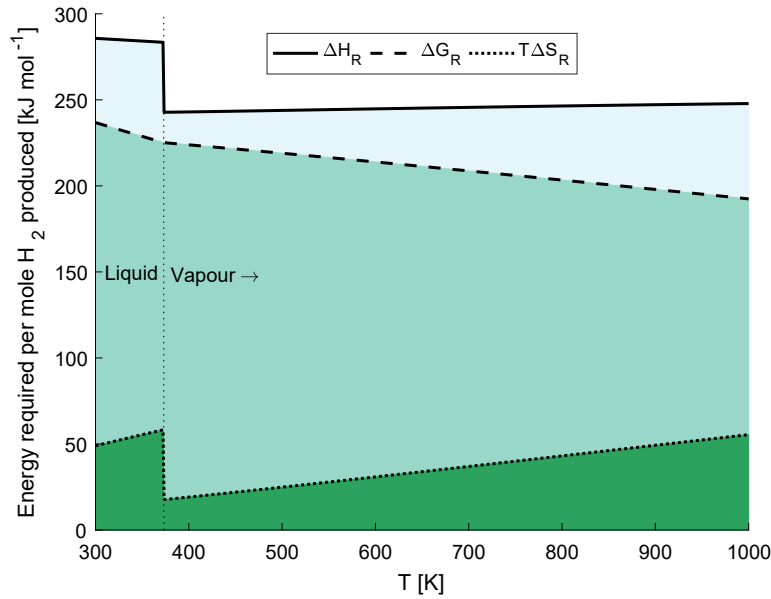


Figure 3.15: The enthalpy, Gibbs energy and heat demand of water electrolysis (1 bar)

If one assumes that the reactant (*i.e.* H_2O) is heated from room temperature (*i.e.* 25 °C) to the electrolysis temperature T and the products are cooled back to room temperature, then the standard solar to fuel efficiency which uses the Gibbs energy of the hydrogen under standard conditions (leading to a minimum cell potential of 1.229 V) is used:

$$\eta_{STH} = 1.229[V]j_{photo}\eta_f/I_{solar}.$$

A system where the PV and the electrolysis system are in thermal equilibrium (*i.e.* at the

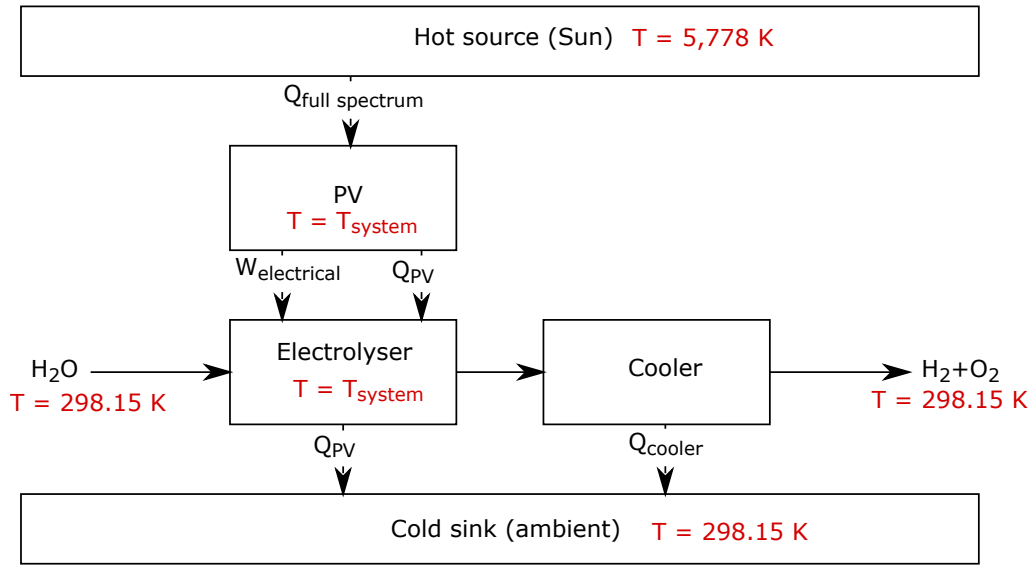


Figure 3.16: Thermodynamic diagram of heat and work flow through a hybrid PV-thermal-electrolysis system where the PV system is in thermal equilibrium with the electrolyser

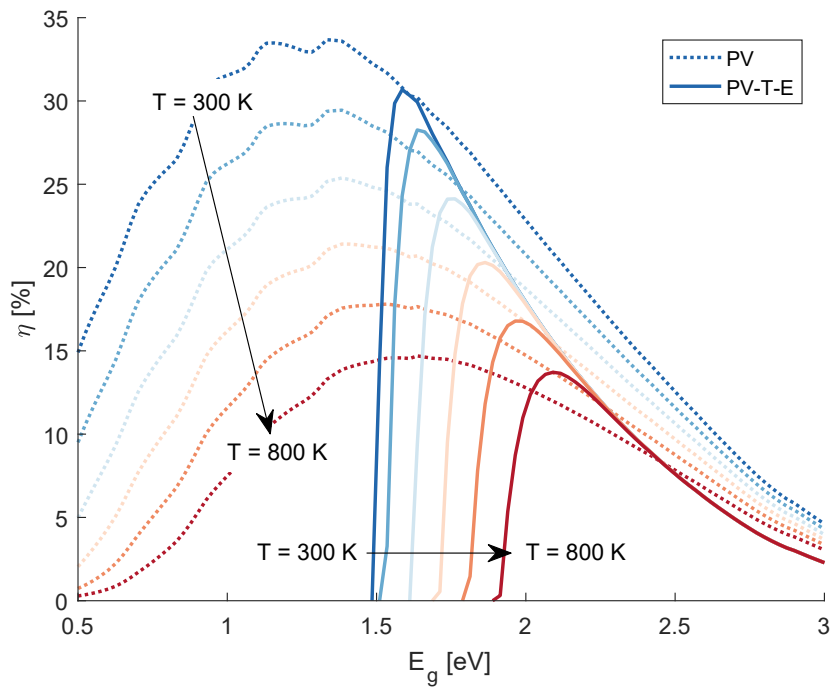


Figure 3.17: Limiting efficiency of a system where the PV and electrolyser are at the same temperature ($T = 300, 400, 500, 600, 700, 800 \text{ K}$, $S = 1$)

same temperature) can be represented by the thermodynamic diagram shown in Figure 3.16. The design of this would likely be similar to conventional PV-T technologies, where a range of commercial collectors and prospective designs exist in the literature [98–101]. Figure 3.17 demonstrates that, for this system, increasing the temperature only serves to reduce the thermodynamic limiting efficiency. It is also important to note that at the higher temperatures studied (*i.e.* up to 800 K), whilst the detailed balance equations can assume that the semiconductor material is still capable of extracting charge, in reality these materials will cease to function at such high temperatures making the thermodynamic limit even more unachievable. Furthermore, the majority of conventional PV-T designs [98–101] would not be able to reach these high temperatures and hence this study is primarily a theoretical one for hypothetical designs.

At smaller temperature increases, this type of system may have a positive effect on the realistic efficiency though the improvement of the kinetics. Consequently, this potential efficiency improvement can be realised by achieving a larger fraction of the thermodynamic efficiency, albeit with a reduced limiting efficiency.

If, on the other hand, a temperature differential between PV and electrolyser is created and heat is supplied from the solar photons to create a system where electrolysis occurs at a higher temperature (see Figure 3.18), efficiencies can surpass that for systems with no temperature difference (see Figure 3.19). Essentially, this means that some of the solar energy normally wasted as heat can be captured in the free energy of the products. Such a system which operates at higher than ambient temperature will be required to supply the heat of reaction and the heat required to raise the temperature of the reactant, water (see Eq. (3.21)).

$$Q_h = \begin{cases} \int_{T_{amb}}^T C_{p,H_2O,l} \dot{n}_{H_2O} dT, & T < 373.12[K] \\ \int_{T_{amb}}^{T_{vap}} C_{p,H_2O,l} \dot{n}_{H_2O} dT + \Delta H_{H_2O}^{vap} \dot{n}_{H_2O} + \int_{T_{vap}}^T C_{p,H_2O,g} \dot{n}_{H_2O} dT, & T > 373.12[K] \end{cases} \quad (3.21)$$

For any such system to operate with a temperature difference between ambient and electrolysis, heat will be required which could be met by conversion of a portion of the solar photons into heat. If this heat is provided by sub-bandgap photons, the amount of heating power that can be provided per area is shown in Figure 3.20. It must be noted that the heat generated by thermalisation to band edge in the PV material will be provided at the PV temperature, and if this is intended to be significantly lower than the electrolysis temperature, this heat is unusable and will be lost to ambient. The sub-bandgap photons can be captured at a different temperature to the PV material as they could be absorbed by a material thermally insulated from the PV. The heat

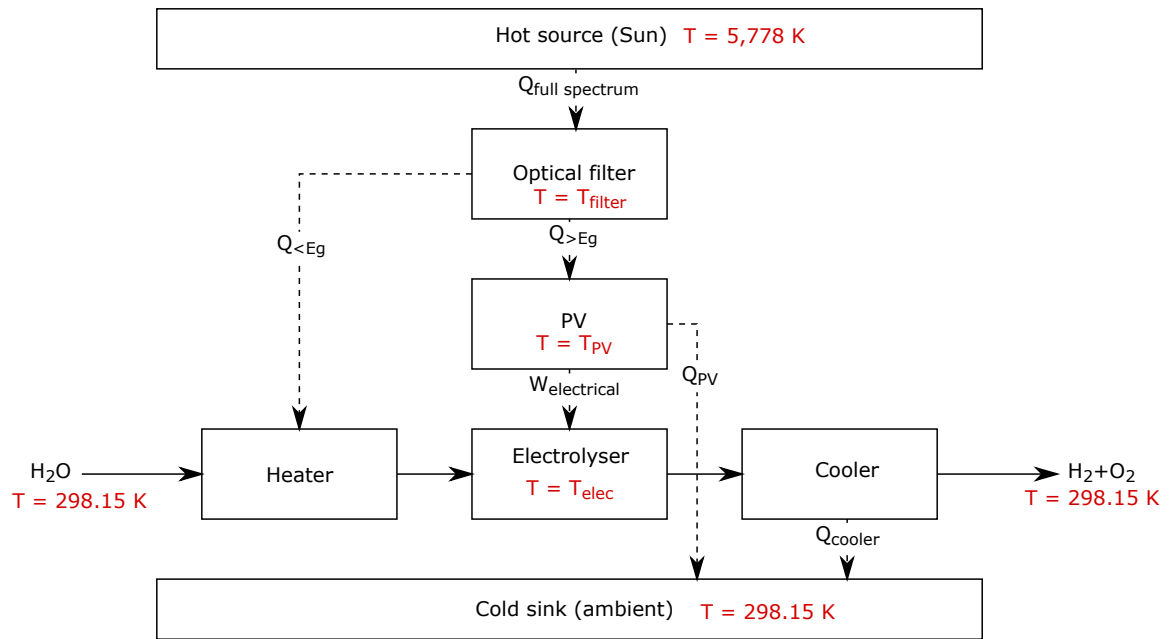


Figure 3.18: Thermodynamic diagram of heat and work flow through a hybrid PV-thermal-electrolysis system operating with a temperature differential between PV system and electrolyser

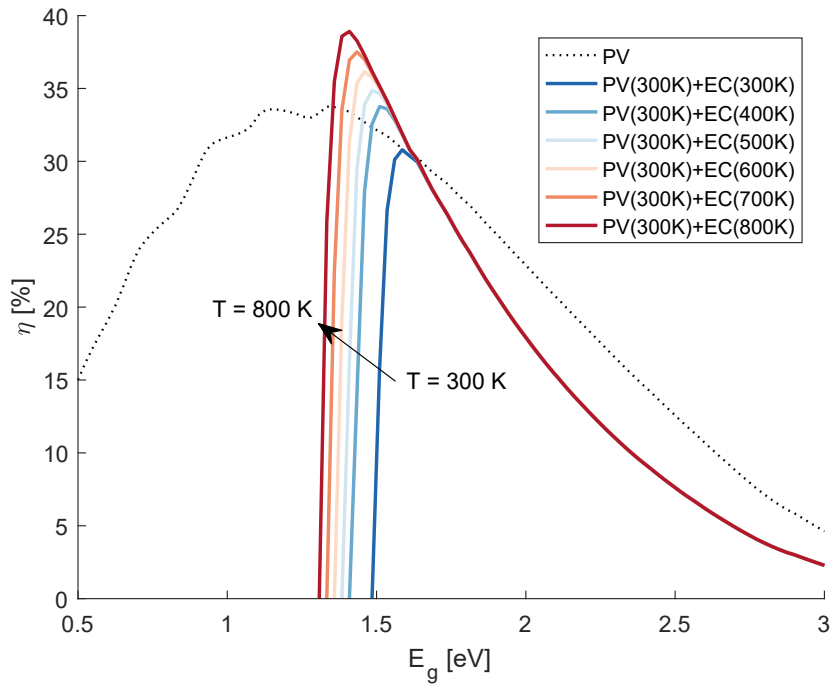


Figure 3.19: Limiting efficiency of a system ($S = 1$) where the PV is at ambient temperature and the electrolyser is at $T = 300, 400, 500, 600, 700, 800$ K

requirement per mole of water temperature rise and reaction can be seen in Figure 3.21. The heat required and the heat supplied can be compared in order to elucidate whether there is enough energy sub-bandgap in order meet the demand and it can be seen in Figure 3.22, there is enough energy sub-bandgap in the ideal case (which assumes no heat loss). Therefore, such a high performing device is thermodynamically possible, albeit potentially very difficult to realise.

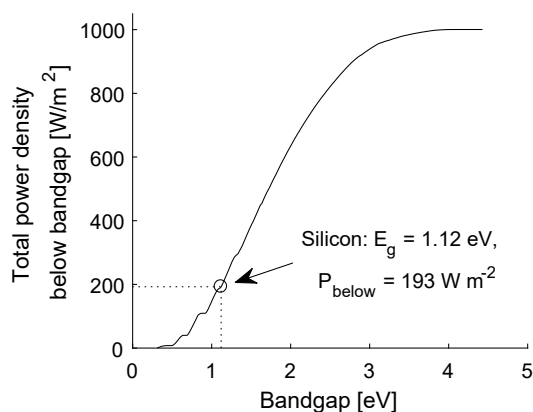


Figure 3.20: Total power density below bandgap for standard AM1.5G solar spectrum

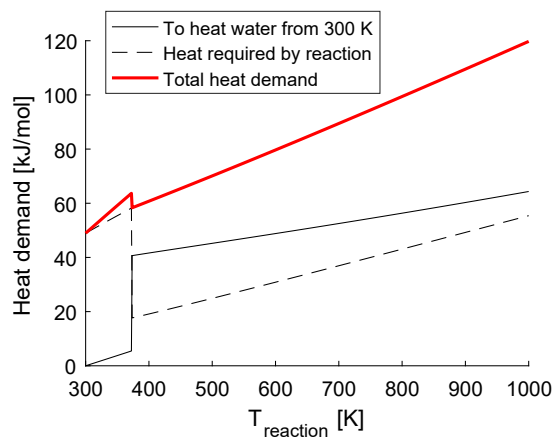


Figure 3.21: Heat requirements for reaction and reactant temperature rise

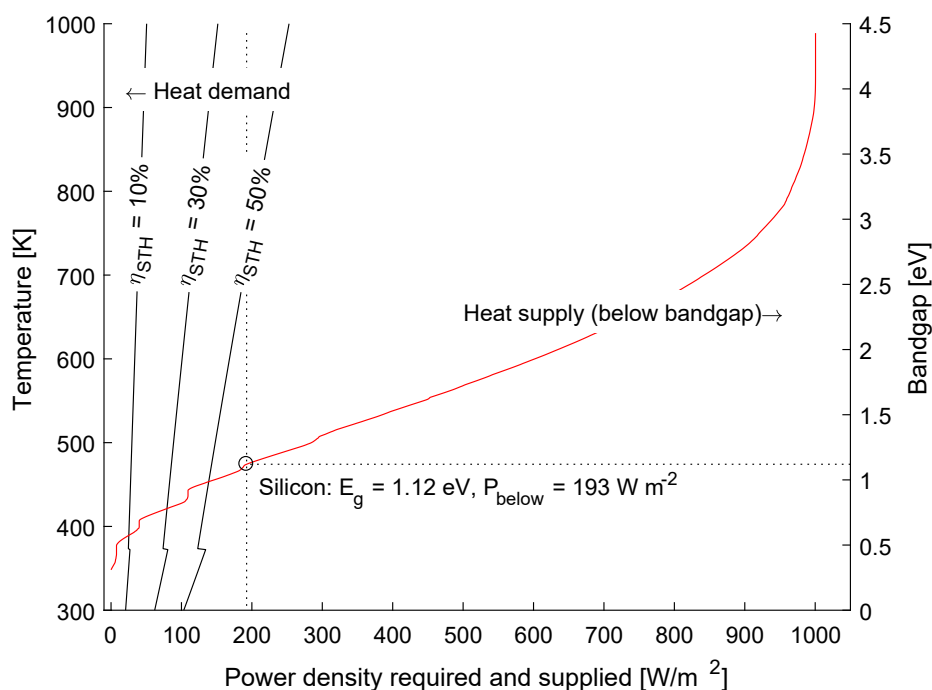
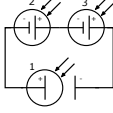
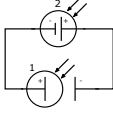
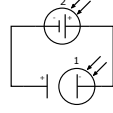
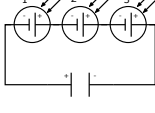
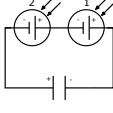
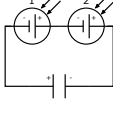
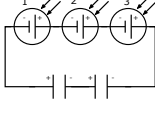


Figure 3.22: Total heat demand (reaction and heating) *vs.* available heat supply (from sub bandgap photons)

3.6 Comparison of experimental results to limiting efficiencies

Just as one can compare the performance of different heat engines at different temperatures by looking at the ratio of achieved thermal efficiency to limiting (Carnot) efficiency, one could compare PEC devices in a similar way. The ratio of achieved STH efficiency to fundamental limiting efficiency will give a measure of the *extent of realised potential*. As a case study the following studies found in Table 3.5 will be compared.

Table 3.5: Case study literature for comparison with limiting efficiency. The nomenclature for the type of device is: PV+PEC = PV biased PEC, i-PV+E = integrated PV + electrolysis, e-PV+E = external/separated PV + electrolysis

No.	Type	Electrical config.	Optical config.	Materials	η_{STH}	Ref.
1	PV+PEC		$\rightarrow 1 \rightarrow 2 \rightarrow 3$	1) BiVO ₄ 2) a-Si:H 3) nc-Si:H	5.2%	[83]
2	PV+PEC		$\rightarrow 1 \rightarrow 2$	1) WO ₃ 2) DSSC	3.1%	[102]
3	PV+PEC		$\rightarrow 1 \rightarrow 2$	1) GaInP ₂ 2) GaAs	12.4%	[84]
4	i-PV+E			1) CIGS 2) CIGS 3) CIGS	10.0%	[85]
5	i-PV+E		$\rightarrow 1 \rightarrow 2$	1) GaInP ₂ 2) GaAs	16.5%	[43]
6	i-PV+E		$\rightarrow 1 \rightarrow 2$	1) AlGaAs 2) c-Si	18.3%	[103]
7	e-PV+E		$\rightarrow 1 \rightarrow 2 \rightarrow 3$	1) InGaP 2) GaAs 3) GaInNAsSb	32.5%	[49]

Note that in Table 3.5, the achieved efficiency for Jia *et al.* [49] has been corrected

from 31.2% to 32.5% as the electrolyzers operated above room temperature at 80°C where the minimum voltage required falls to 1.18 V. To compare on an equal basis, the hydrogen produced was assumed to be at 25°C (cooled from 80°C) and therefore the efficiency was corrected to $31.2\% \times 1.23 \text{ [V]}/1.18 \text{ [V]} = 32.5\%$.

The bandgaps were extracted from each paper or estimated, as shown in Table 3.6. For study number 2 (Brillet *et al.* [102]), the top cell was assumed to be limiting which was achieved by assuming a bottom cell bandgap of less than *ca.* 2.1 eV. From this, and assuming a temperature of 25°C for all studies except study 7 (80°C electrolyzers, 25°C PVs), and assuming AM1.5G, the maximum efficiency for the given bandgaps and configuration $\eta_{STH,max}$ and the global maximum efficiency for optimal bandgaps $\eta_{STH,global \text{ max}}$ are calculated.

Table 3.6: Bandgaps and STH efficiencies for all of the selected studies. Where data was incomplete, reasonable values for bandgaps were assumed (denoted by brackets). The subcell which is current limiting is denoted in red bold font.

	Study number						
	1	2	3	4	5	6	7
$E_{g,1}$ [eV]	2.4	2.6	1.83	1.2	1.83	1.6	1.895
$E_{g,2}$ [eV]	(1.7)	(<2.1)	1.42	1.2	1.42	1.1	1.414
$E_{g,3}$ [eV]	(1.1)	-	-	1.2	-	-	0.965
η_{STH} [%]	5.2	3.1	12.4	10.0	16.5	18.3	32.5
$\eta_{STH,max}$ [%]	9.2	6.2	16.3	16.4	16.3	23.1	37.4
$\eta_{STH,global \text{ max}}$ [%]	25.0	39.8	39.8	23.9	39.8	39.8	49.6

Figure 3.23 shows the actual efficiency *versus* the theoretical limiting efficiency of the configuration. As expected, for all studies the achieved efficiency η_{STH} is less than the maximum efficiency $\eta_{STH,max}$ except for study number 5 and this discrepancy will be discussed later. Figure 3.24 displays the fraction of efficiency achieved relative to the maximum and global maximum for each of the experimental demonstrations. This type of metric is comparable to an exergy efficiency as outlined in Chapter 2, and signifies the realised potential of a given experimental device.

Firstly, as expected the higher performance materials such as III/V semiconductors realise a greater proportion of the limiting efficiency, than the lower performing materials such as Si, DSSC and metal oxides. This figure of merit indicates the extent to which the semiconductor and catalysts used in the experiment approximate the ideal semiconductor material and electrochemical interface: loss-less transport, no

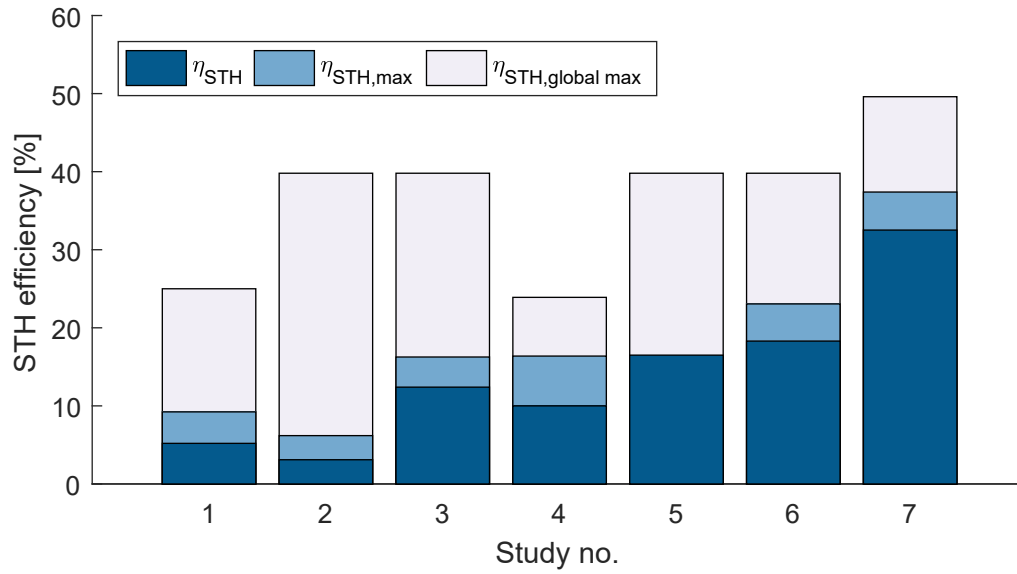


Figure 3.23: Bar graphs showing for each study the experimentally achieved STH efficiency, the maximum efficiency for the configuration, and the maximum efficiency for the configuration assuming optimal bandgaps.

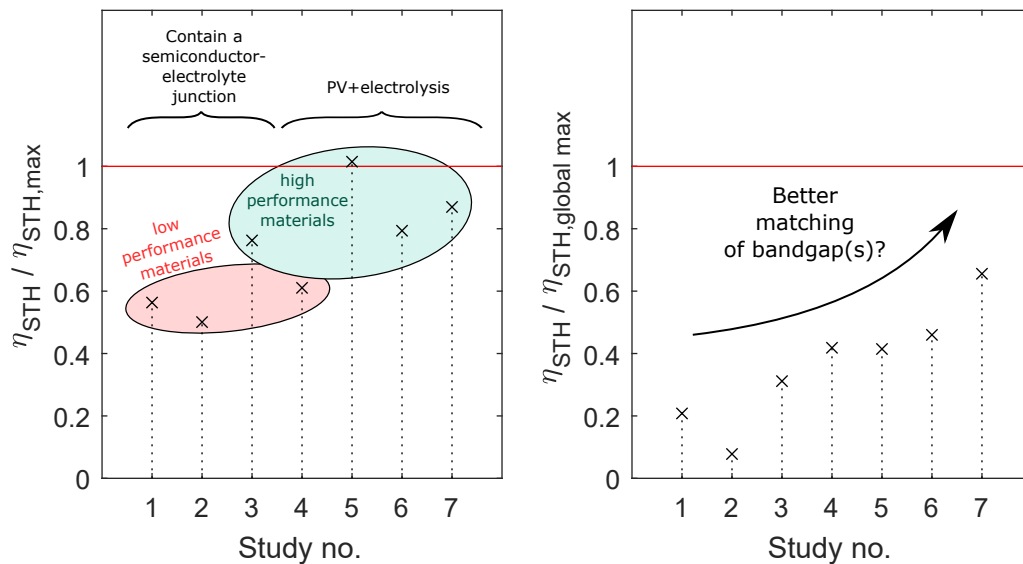


Figure 3.24: The realised potential of each of the studies with respect to the maximum efficiency for the configuration (left), and the maximum efficiency for the configuration assuming optimal bandgaps (right).

recombination other than unavoidable radiative, and instantaneous reaction kinetics. The second observation is that the PV + electrolyser designs (no. 4-7) realise the greatest fraction of the global maximum compared to designs with a PEC interface. This is likely due to the fact that for a PEC interface to be stable in the electrolyte it generally requires a large bandgap which in turn limits the amount of solar energy that can be captured [23].

Returning to the issue of study no. 5 (Khaselev *et al.* [43]) and by association, study no. 3 (Khaselev and Turner [84]), either the maximum limiting efficiency calculated is incorrect or the experimental result is wrong. The small changes in the bandgaps given for the bottom cell which is current limiting will have a big influence on the calculated limiting efficiency. For example, $\eta_{STH} = 16.5\%$ was reported along with bandgaps of 1.83 eV and 1.42 eV which corresponds to a $\eta_{STH,max} = 16.3\%$. If the reported 1.42 eV was inaccurate and instead 1.40 eV is used to calculate the limiting efficiency, a result of $\eta_{STH,max} = 17.3\%$ is found which is now more than the experimental result. Furthermore, the model assumes complete absorption of above bandgap whereas if the top cell lets through a fraction of above bandgap light, the limiting efficiency could be increased (this approach of decreasing the top absorber thickness has been previously discussed by Seitz *et al.* [65]). Finally, this discrepancy could also be due to an over reported STH efficiency calculated based on the current flowing and not the actual molar rate of hydrogen production. Furthermore, the device appears not to contain a membrane and therefore it is possible that the back reaction of H₂ and O₂ could reduce the faradaic efficiency.

Additionally, this analysis emphasises that Jia *et al.* [49] achieved such impressive STH efficiencies not only through use of state of the art high performance solar cells but through the optimisation of the electrical and optical configuration which matched the total photo-voltage produces to the voltage required to drive electrolysis.

Therefore, this analysis clearly demonstrates the significance of the conceptual configuration of the device on the resulting performance. In future work we intend to conduct a larger review in order to elucidate trends and progress in the field of solar water splitting, particular the degree to which improvements are driven by more ideal configurations compared to semiconductor material developments or catalytic improvements.

3.7 Future extensions to the model

The model outlined in this chapter, whilst significantly better than a ‘1st law’ type analysis, makes a number of simplifying assumptions and can only calculate limiting efficiency rather than practical efficiencies. The code is easily extendible and could

be modified to include the realistic performance of solar cells and electrolyzers [64, 67, 68]. The effects of nanostructuring on the optical concentration [104], radiative coupling of sub-cells [64], incomplete absorption of above bandgap photons [65], or carrier multiplication [75] could all be accounted for and easily incorporated into the model.

3.8 Conclusions

- There has been little investigation into the limiting efficiency of unorthodox PEC architectures such as those outlined by Kim *et al.* [81] and Niu *et al.* [82]. Furthermore, the only available open source tool for PEC efficiency calculation is restrictive in the allowable designs.
- Therefore, a thermodynamic model is described in order to calculate the thermodynamic limiting efficiency. This involved a ‘detailed balance’ type model of solar quantum energy converters and non-linear circuit analysis.
- This unifies and extends previous work on the fundamental limiting efficiency for permutations of PEC design and packages this in a freely accessible and extendible open-source code.
- The utility of this code is demonstrated through several examples which include the optimal bandgap calculation for an ideal PEC system in various optical and electrical configuration (up to 3 photo-absorbers).
- A number of ways to achieve a high limiting efficiency can be investigated. This includes the judicious matching of photo-voltage to the electrochemical load, and hybrid systems operating at a temperature differential between photon capture and the water splitting reaction.
- The model and software was then used to critically analyse selected experimental reports of unassisted water splitting devices. It is discovered, as expected, that high performance semiconductor materials such as III/V semiconductors realise a significant proportion of the limiting efficiency. Furthermore, this type of analysis reveals that the significant efficiency improvements made by Jia *et al.* [49] were considerably driven by the optimisation of device configuration.

Chapter 4

Elements of photo-electrochemical reactor design

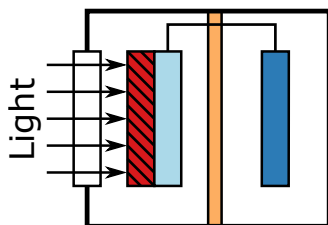
A methodical analysis of the design of photo-electrochemical reactors is conducted comprising of three parts; 1) a classification framework is proposed 2) the design challenges of designing a large scale PEC reactor are summarised 3) a critical literature review of PEC reactor designs.

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[5] Holmes-Gentle, I., Alhersh, F., Bedoya-Lora, F. E. & Hellgardt, K. "Photoelectrochemical reaction engineering for solar fuels production".

in:

N. D. Sankir, M. Sankir, *Photoelectrochemical Solar Cells*, Scrivener-Wiley, 2018



4.1 Classification framework for PEC reactor design

As outlined in the previous chapter, the conceptual configuration of the PEC device determines the limiting efficiency of the process. For any such conceptual design there may be a multitude of ways to engineer a PEC reactor, and hence the reactor design is considered distinct from the conceptual configuration. Here in this section, a classification framework for the physical reactor design is outlined in the following order.

1. Conceptual design (see previous chapter)
2. Construction of electrodes/electrochemical interfaces
3. Physical placement of electrodes and photo-absorbers
4. Electrolyte environment and operating conditions
5. Optical design of reactor
6. Product separation and collection
7. Reactor transport phenomena

Unfortunately, when designing a PEC reactor this classification cannot be a step-by-step design guide (*i.e.* followed sequentially), as considerations from each classification section must be considered simultaneously. For example, the optical design of the reactor will influence and be influenced by the physical placement of reactor components. In the following sections, each item in the reactor classification will be discussed in turn, noting the challenges and issues associated with each.

4.1.1 Construction of electrodes/electrochemical interfaces

An electrochemical interface is comprised of an electrode (an electronic conductor) in contact with an electrolyte (an ionic conductor). In a complete cell, an oxidation reaction will occur at the *anode* and a reduction reaction occur at the *cathode*, ensuring the total charge balance of the system. Any electrodes can be categorised by their electrical polarity or electrical polarities. For example, a electrode with a single polarity (*i.e.* anodic *OR* cathodic) is termed *mono-polar*. If the electrode has both polarities (*i.e.* anodic *AND* cathodic) it is called a *bi-polar* electrode. Electrode geometry can be divided into two broad classes: 1) Flat ‘sheet’ electrodes are macroscopically planar (*i.e.* a flat 2D surface), though may be microscopically rough. 2) Granular particulate systems are made up of many particles which all incorporate both anodic and cathodic sites on the same particle (*i.e.* intrinsically bi-polar). This can be seen in Figure 4.1 where the concepts of mono-polar/bi-polar and planar/particulate can be seen.

If the electrode incorporates a photon-absorption process, this further complicates the categorisation. If the charge excitation and separation process occurs in a semiconduc-

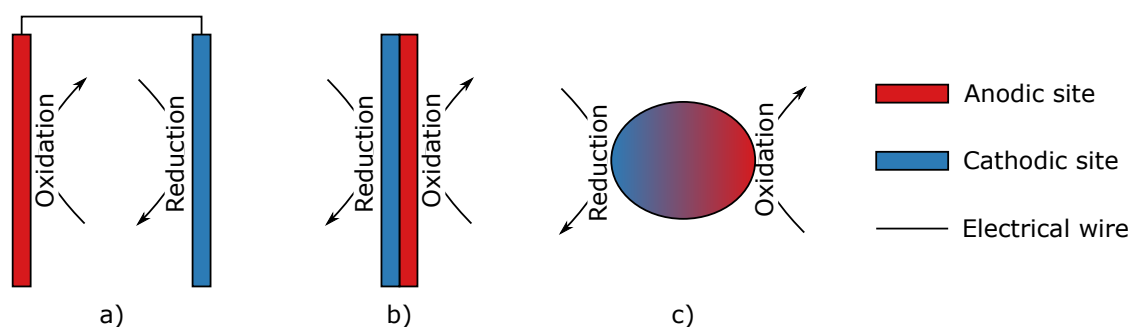


Figure 4.1: a) mono-polar ('wired') planar electrodes b) bi-polar planar electrodes c) bi-polar particulate electrodes

tor material in contact with the electrolyte, a *semiconductor-electrolyte junction* is formed. If the charge carriers are excited and separated in a semiconductor-semiconductor junction (e.g. p-n junction) and then subsequently transferred *via* electronic conduction to the material at the electrochemical interface, this is termed as a '*buried*' junction approach. When the solar cell junction is 'buried' in the electrode, semiconductor materials that are not stable in the electrolyte can be used, as it can be shielded by a protective transparent catalytic layer (e.g. TiO_2 thin film) [105]. However, the efficacy of this approach is an active research topic and there is much debate on whether overcoming the challenge of long term stability is achievable.

The electrode may be composed of one single material, but more commonly multiple materials each fulfilling one particular requirement (e.g. an electrochemically active site, electronic conduction of charges, mechanical strength, photon absorption *etc.*). For example, an electrode may be mechanically self-supporting or deposited, often in a thin layer, onto another mechanically supportive material. Furthermore, the active electrochemical interface may be at a so called *electro-catalyst*, but for reasons of perhaps expense or electronic conductivity, the electro-catalysts is deposited on an electronically conductive substrate. Photo-electrodes are nearly always a composite, where the semiconducting material is placed on a compatible conductive substrate (as a 'back contact') which can be either a metal (e.g. Ti, Fe), conductive carbon, or a transparent conductive oxide film on glass (Fluorine doped Tin Oxide).

4.1.2 Physical placement of electrodes and photo-absorbers

As previously mentioned the construction of electrodes can be broadly classified into two configurations: 1) monolithic 2) bi-polar. This will have ramifications on the physical placement within the reactor and examples of this can be seen in Figure 4.2. The placement of bi-polar electrodes will, by virtue of design, be straightforward as the anodic and cathodic reaction sites cannot be moved independently. Therefore, for

planar electrodes, bi-polar electrodes are placed as a *monolithic* stack (*cf.* Fig. 4.2a, 4.2b). As there must be more than one mono-polar electrode in order to complete an electrochemical cell and each are spatially distinct from one another, there will be greater choice of electrode placement (*cf.* Fig. 4.2c, 4.2d).

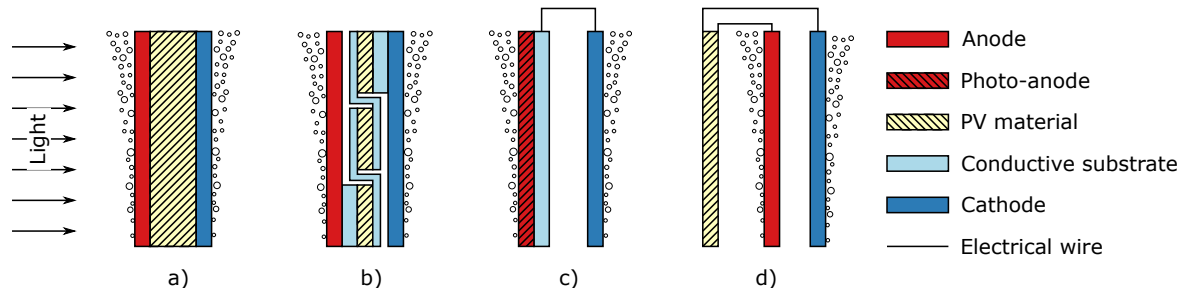


Figure 4.2: Four examples of electrode placement a) Wireless monolithic b) Wired monolithic c) Mono-polar with integrated photo-absorber d) Mono-polar external PV bias

An additional classification of the electrode placement could be made according to how the current is collected and flows through the electronic conductors of the cell. In a *wired* cell, current is collected over the entire surface of the electrode and then transferred *via* an electronic conductor to the opposing electrode. In a *wireless* cell, each stacked layer is electrically bonded to one another and the current flows directly from one electrochemical surface through the conductive substrate/PV material and through to the opposite electrode. Commonly, the mono-polar designs in Fig. 4.2c and 4.2d are commonly referred to as ‘wired’, and whilst this is correct, it is possible to describe a ‘wired’ (by our definition) monolithic device as shown in Figure 4.2b. Such a configuration would not normally be called ‘wired’ so therefore to avoid confusion we will stick to the terms *monolithic bi-polar*, *particulate bi-polar* and *mono-polar* when describing electrode configuration as this distinction will have the greatest impact on the overall design. These choices impact the path length of ionic charges between anodic and cathodic reaction sites which in turn impacts the ohmic losses (*i.e.* voltage lost to resistive heating). As pointed out by Newman, due to the typically low electrolyte conductivity relative to electronic conductors, priority must be given to minimise the ionic path length [106]. An example of this for a bi-polar electrode, would be perforations of a planar electrode in order to reduce the ionic path length [107–109].

If the electrochemical cell is being biased by an external solar cell (rather than an semiconductor-electrolyte junction), the PV absorber can be either a ‘buried’ junction as part of a monolithic stack or completely separate, an approach which is commonly referred to as *PV + electrolysis*. Both configurations are shown in Figure 4.2a and 4.2d. From an engineering perspective, scaling up PV + electrolysis systems constitutes a significantly simpler design challenge when compared to an integrated PEC designs, as

the light absorption and charge excitation process can be optimised separately to the electrochemical reactor.

The current concentration ratio F is defined in Eq. (4.1) as the ratio of the geometric projected electrode area to the photo-absorber area [110]. For the vast majority of ‘integrated’ PEC systems (*cf.* Fig. 4.2a-c) this will be constrained to unity, whereas for PV + electrolysis (*cf.* Fig. 4.2d), gains in efficiency and reduction in speculative cost can be made by respectively increasing and decreasing the current concentration ratio [111, 112].

$$F = A_{\text{electrode}}/A_{\text{photo}} \quad (4.1)$$

4.1.3 Electrolyte environment and operating conditions

The choice of electrolyte and operating conditions may influence the PEC reactor design in a number of ways. Firstly, the electrolyte must be conductive and is therefore either an acidic, basic or buffered solution. Less conductive electrolytes lead to higher ohmic losses for current passing through the electrolyte, but conversely, the most conductive electrolytes are often corrosive to the semiconducting materials. In order to ascertain material stability, Pourbaix diagrams are useful for assessing the most thermodynamically stable state at a given electrode potential E and pH [113].

The pressure and temperature of the system will dictate the phase of the reactant and products. High temperature systems may require some sort of heat management system (such as a cooling fluid in concentrated solar systems), and systems operating at any pressure above ambient will require mechanically stronger reactor designs. If the pH of the electrolyte is near neutral (~ 7 pH), the system may require the forced convection (*i.e.* pumping) of the electrolyte in order to minimise the issue of developing pH gradients [114]. Additionally, forced convection may resolve mass transfer issues, perhaps due to low concentration of a reactant. For liquid water splitting, reactant mass transfer will not be limiting. There are a few example of higher temperature water vapour splitting using a solid electrolyte in a membrane electrode assembly similar to a fuel cell [115, 116].

Besides water splitting, there are many other reactions that could be driven photo-electrochemically and this may change the reactor design. For example, the oxygen evolution reaction (OER) could be replaced with an alternative oxidation reaction [117–119] which may be favourable due to a decrease in the required thermodynamic electric potential, kinetic improvements or an improved product value. Use of high value ‘hole scavengers’ such as methanol are not energetically or economically justified for a large scale process, as a complete life cycle analysis would demonstrate. However,

the economic revenue from cleaning a waste stream containing material requiring oxidation, such as H_2S [117], may greatly improve the economics of such a photo-electrochemical process. Careful engineering would be required for reactants that are dilute in order to minimise mass transport issues, and the optical design of the reactor may have to be altered for reactants that absorb useful portions of the solar spectrum (water transmits the majority of visible light [120]).

4.1.4 Optical design of reactor

A integrated PEC reactor design must physically contain the electrolyte and gaseous products from the surroundings, whilst also allowing sunlight to enter the reactor. It will therefore require that at least part of this structure is transparent, and designs can therefore be classified by the number of optical apertures (*i.e.* number of windows). As PV + electrolyser systems separate the capture of the photon's energy and the use of that energy to drive a electrochemical reaction in the dark, there is no optical design of the electrochemical reactor required.

Figure 4.3 shows example designs with a single window (Fig. 4.3a-c), and a design with two windows (Fig. 4.3d). The majority of designs proposed to date are single aperture reactors, but there are a number of two windowed designs discussed in the literature [121, 122] and these would require additional focusing optics (mirrors).

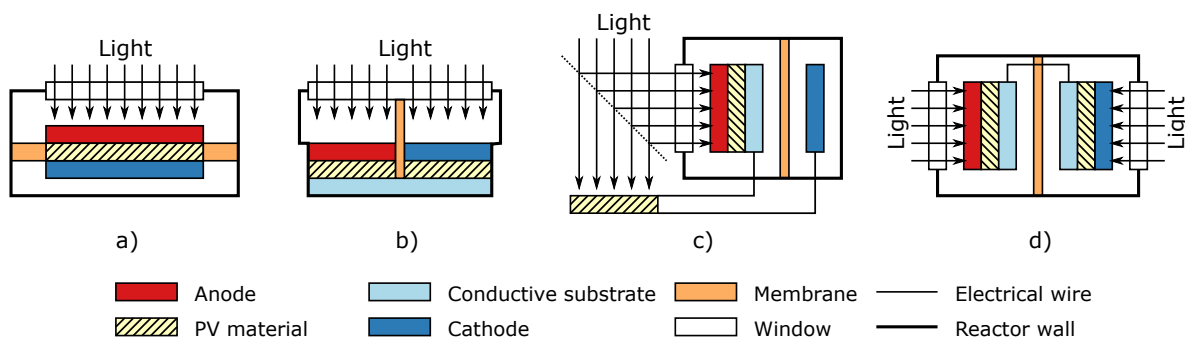


Figure 4.3: Four example optical designs showing single aperture (a,b,c) and two aperture (d) designs. Example c) employs a dichroic (spectrum splitting) mirror to split the light into two paths leading to more efficient utilization of the spectrum

Whilst there are a vast number of non-imaging optical designs for capturing solar energy, of which may include optical components such as lenses, mirrors and spectral splitting, an overarching parameter can be defined: the irradiation concentration ratio C . This is defined in Eq. (4.2) as the ratio of the geometrical area of the concentrating optics to the photo-absorber area.

$$C = A_{conc}/A_{photo} \quad (4.2)$$

4.1.5 Product separation and collection

In the case of water splitting, the gaseous products (H_2 & O_2) must be collected and removed from the reactor. The complete separation of products is of paramount importance due to the lower flammability limit of hydrogen in pure oxygen (LFL = 4 vol%), and the undesirable impact of pre-mixed gas combustion potentially resulting in an explosion. If both oxidation and reduction products are co-evolved, there will be issue around 'cross-over' where the back reaction occurs hence reducing the faradaic efficiency. Furthermore, co-evolution requires separation of H_2 from O_2 , which is incredibly energetically expensive.

In order to achieve an acceptable product separation during operation, a number of technologies can be employed:

1. Ion selective transport membrane
2. Porous separator (not ion selective)
3. Membrane-less hydrodynamic separation
4. Redox mediator

The first, an ion selective transport membrane such as Nafion®, is the most commonly discussed in water splitting due to its low cross-over rates and proven safety record in polymer electrolyte membrane electrolysis. Unfortunately, such ion selective membranes can be expensive, and particularly for alkaline conditions which require an anion exchange membrane (as opposed to a proton exchange membrane) where long-term stability is a challenge.

A porous separator operates by allowing the diffusion of all species (non-selective) through a tortuous path through the porous membrane. It is commonly used in the chloralkali process and alkaline electrolysis where it is an established technology (*e.g.* asbestos or polymer diaphragm). Porous separators will be inexpensive and typically have a higher effective conductivity relative to membranes, but gas cross-over will occur at higher rates and so care must be taken to ensure acceptable levels of dissolved gas cross-over [123].

A membrane-less hydrodynamic separation system could be achieved through hydrodynamic control of products. These separated products could be dissolved [1] or as gaseous bubbles [124, 125]. The removal of the membrane would be advantageous in removing a source of energetic loss and economic cost from the reactor. However, due to the relative immaturity of such technology, extended operation is required in order to demonstrate an acceptably low risk of explosion before these technologies can be implemented.

Redox mediators can also be used as a product separation methodology. The water splitting reaction can be divided into two redox reactions linked together with reversible

redox shuttles such as IO_3^-/I^- . This is particularly practical approach for eliminating co-evolution of H_2 and O_2 in particulate systems. Such two-step photo-excitation systems are termed *Z-scheme* [126, 127] though may suffer from significant faradaic losses if the poor selectivity of catalyst drives the backward reaction [128]. Solid state redox mediators would remove this back reaction typical to aqueous phase (hence mobile) redox mediators as demonstrated by the work of Landman *et al.* who evolved H_2 and O_2 in a two-step process by charging and discharging a $\text{Ni}(\text{OH})_2/\text{NiOOH}$ counter electrode [129]. Furthermore, decoupling H_2 from O_2 generation could facilitate hydrogen evolution under pressure which may reduce the required downstream gas compression costs [130]. It is important to note that the redox mediator approach typically removes the ohmic losses associated with the membrane, and replaces it with the kinetic losses associated with the redox mediator forward and backward reactions.

Designs that employ membranes have to compartmentalise the anodic and cathodic chambers without negatively impacting the light reaching the photo-absorbers. As these membranes are not typically optically transparent, they must be placed in the reactor so as not to block the incoming light and example placements can be seen in Fig. 4.3. If a membrane is used, a key parameter, M , is defined in Eq. (4.3) as the current density ratio between membranes and electrodes. This is a useful parameter as the ohmic losses will be proportional to current densities flowing through the membrane and so ohmic losses decrease with increasing M , and the capital cost of membrane will increase with increasing M .

$$M = A_{\text{membrane}}/A_{\text{electrode}} \quad (4.3)$$

4.1.6 Reactor transport phenomena

Most demonstrations of photo-electrochemical water splitting are laboratory scale and performed in batch (*i.e.* a closed system), and hence the concentration of species within the reactor will change over time. For any feasible large scale systems, it likely such a design must continually remove products and ‘top-up’ reactants. In this case, the fluid mechanics of the pumped electrolyte and evolved gases must be considered [131–133]. Additionally, recirculation of the electrolyte will have the advantageous effect of higher mass transfer rates, faster removal of gas bubbles and greater temperature control.

4.2 Is there a linear progression between integrated device and PV + electrolysis?

As mentioned by a number of authors [47, 134], a gradual transition can be seen between a fully integrated PEC system and a completely separated PV + electrolysis system. This is shown in Figure 4.4, and whilst a useful abstraction will not be used for this discussion as the strength of this analysis, its simplicity, is also its weakness. Some reactor designs prove particularly hard to place on this scale, such as particulate systems or systems with multiple light absorbers or with spectral splitting optics (*cf.* Fig. 4.3c which has both an external PV and a photo-anode).

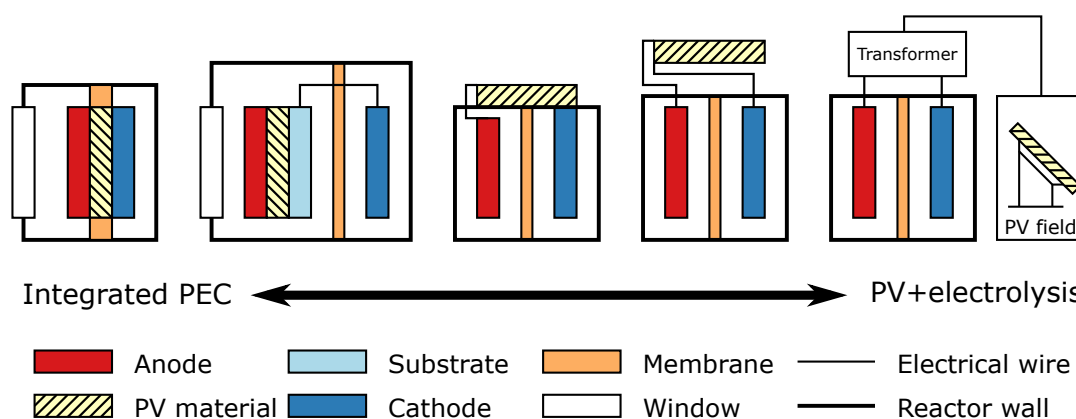


Figure 4.4: Example reactor designs demonstrating the gradual transition between integrated PEC and PV + electrolysis for single photo-absorber systems

4.3 Challenges of PEC reactor scale up

Engineering large scale PEC reactors is a significant design challenge and it is complicated further by the vast combination of conceptual designs being proposed. Each conceptual design will have a suitable reactor design, and so there have been a correspondingly diverse array of reactor designs in literature. Coupled with the various inherent compromises that must be made when tackling the challenges outlined here, no consensus has been or likely will be established for a standardised PEC reactor design.

It is therefore instructive to abstract the individual design challenges and for clarity, these have been grouped together by their relevant conserved quantity. For example, light reflection from bubbles hinders the photon transfer in the system and is grouped accordingly. It may be useful to note that many of these challenges in reactor design are tackled in other more established fields of electrochemical engineering, and so

comparison may be enlightening. A full list of the intrinsic challenges of PEC reactor design can be found in Table 4.1.

Table 4.1: Engineering challenges for scaling up PEC reactors

Charge transfer	
Substrate conductivity	Use of low conductivity substrates, such as transparent conductive oxides, may lead to large resistive (ohmic) losses [2, 131].
Electrolyte conductivity	The electrolyte must support the transfer of ionic charge between electrodes and hence be conductive enough to reduce ohmic losses. Therefore, alkaline or acids are typically used, and neutral solutions will be buffered in order to be conductive enough. Furthermore, bubbles evolving on the electrode interface will reduce the local effective conductivity [135].
Membrane conductivity	Any membrane used (for product separation) must allow the transport of ionic charge across it whilst minimising the electric potential lost in the process (ohmic losses), as any extra electric potential required must be provided by the solar cell/photo-electrode [136].
Current density distribution	It is desirable to minimise inactive electrode area and have uniform current density [109, 137]. However, the placement of the electrodes, the reaction kinetics (and any mass transfer kinetics) all impact the current density distribution [138].
Efficient capture of light (quantum efficiency)	This is impacted by a number of material properties, such as the dynamics of charge transfer and recombination within the light absorber and at the interface. As this is primarily not an engineering consideration, this will not be focused upon in the subsequent discussion as the fundamental principles and challenges have already been clearly outlined elsewhere [14, 139–141]
Photon transfer	
Window transmittance	Light must pass as unhindered as possible through the window into the reactor and therefore the transmittance of the window material must be considered. Collated data on relevant window materials can be found in Ref. [142].

Gas evolution		The gaseous bubbles forming at the surface of the photo-electrode will cause a decrease in light transmitted to the photo-absorber due to light scattered at bubbles.
Electrolyte transmittance		Light attenuation <i>via</i> absorption of photons in the electrolyte leads to a reduced amount of light available for conversion in the photo-absorber. For water, this is particularly an issue at higher wavelengths (< 900 nm) [120]. Furthermore, any other dissolved species present, such as aqueous redox mediators or hole scavengers, may absorb visible light more strongly than water.
Mass transfer		
Concentration and pH gradients		Depletion of electrochemical species/reactants and the formation of pH gradients will negatively impact the performance of the cell. This consideration is most challenging for neutral pH electrolytes and batch operation [114, 136]. At higher solar concentration or when the reactant is in low concentrations (<i>e.g.</i> redox mediators, dilute organic waste, vapour phase operation <i>etc.</i>), the current may be mass transfer limited. For concentrated electrolytes this will be <i>ca.</i> 10^4 A m ⁻² [109] (<i>cf.</i> 10% STH at 1 Sun = ~ 8 A m ⁻²).
Product cross-over		In order to prevent the co-collection of both hydrogen and oxygen and potentially explosive mixtures forming, the products must be produced and collected separately. This minimisation of the product 'cross-over' is normally achieved using a membrane. Furthermore, product cross-over is detrimental to the faradaic efficiency as back-reaction is very likely to occur (creating a sufficiently selective electro-catalyst when the back-reaction is thermodynamically favourable is exceptionally challenging).
Momentum transfer		
Electrolyte and gas fluid mechanics		The fluid mechanics of the reactor design will have a significant impact on the mass and heat transfer within the system. Computational Fluid Dynamics (CFD) is common tool used to assess the electrolyte flow patterns [114, 131, 133] or two phase (gas + electrolyte) flow regime [132].

Heat transfer		
Operational	tempera-	The temperature of the PEC reactor will influence the system performance (<i>e.g.</i> increasing the temperature may improve kinetics, increase material degradation, worsen semiconductor performance). Heat accumulation will be a significant issue at higher concentrations of solar irradiance as water absorbs infrared light strongly.
ture		

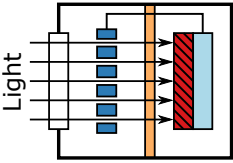
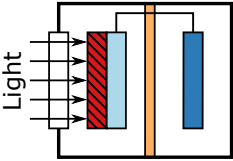
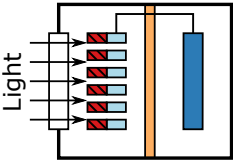
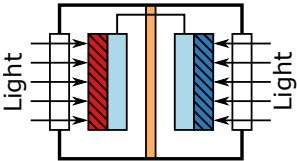
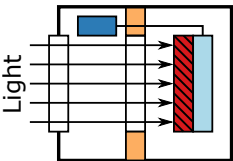
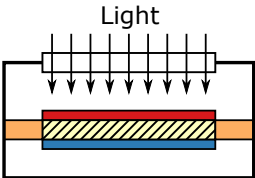
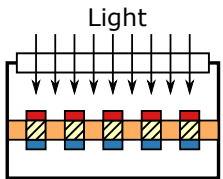
Each engineering aspect given in Table 4.1 cannot be tackled in isolation, as there are many interactions between them. This is a universal design challenge, and typically mathematical optimisation can be used to make compromises between individual design aspects, whilst optimising the design objective function. Often, such an objective function would be to minimise the total delivered cost of H_2 (\$ kg^{-1}), or the cost of CO_2 mitigation. It is therefore informative to identify which design goals are in competition with one another. Such an analysis of the trade-offs in photo-absorber material properties has been made in a book chapter by van de Krol [14, p. 57].

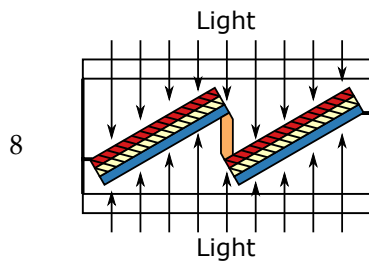
- Minimising membrane ohmic drop $\leftrightarrow$ minimising product cross-over
- Uniformity of the current density distribution $\leftrightarrow$ large area photo-electrodes
- Reducing electrolyte ohmic drop $\leftrightarrow$ Material stability in electrolyte
- An unblocked pathway for light $\leftrightarrow$ placement of components (electrodes, membrane *etc.*) so as minimise ohmic losses and current density distribution non-uniformity
- High H_2 production rates $\leftrightarrow$ mass transfer and kinetic (overpotentials) limitations

4.4 Literature survey of PEC reactor designs

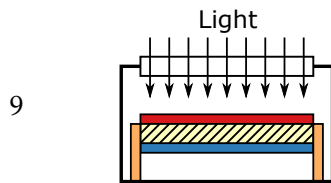
The previous section described the challenges inherent in creating an efficient and scalable design. These issues have been discussed previously and a number of reactor designs proposed and tested. However, there is a great diversity in designs both due to design choices (*e.g.* number of photo-junctions, type of junction *etc.*) and which design challenges are focused upon. Table 4.2 show schematics of selected designs from literature accompanied by some comments on what each design achieves. PEC reactors intended for material development (*e.g.* the ‘cappuccino’ cell [143]) have been specifically excluded from this analysis in order to focus on the engineering challenges of scale up.

Table 4.2: PEC reactors design schematics from literature

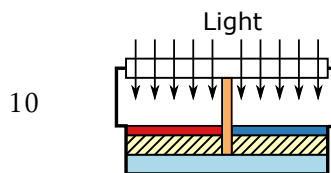
No.	Schematic	Ref.	Notable comments, advantages and disadvantages
1		[131]	• Minimises current density distribution • Cathode and membrane are in the path of the light causing light to be lost. Typical membrane materials are not optically transparent
2		[121] [144] [145]	• Minimises the photon path length to photo-electrode • Serious current density distribution issues
3		[109]	• Similar to Design 2 by with perforations which solve the current density distribution issues • Lost photo-electrode area to perforations
4		[121] [122]	• Serious current density distribution issues • Minimises the photon path length to photo-electrode • Requires optics in order to focus sunlight into the 2 reactor windows
5		[146]	• Similar to Design 1, but cathode and membrane is moved out of the way of the light • Large photon path length to photo-electrode
6		[147] [148]	• Serious current density distribution issues • Potentially large ohmic losses in electrolyte [106]
7		[123] [107]	• Similar to Design 6 by with perforations which solve the current density distribution issues • Lost photo-electrode area to perforations



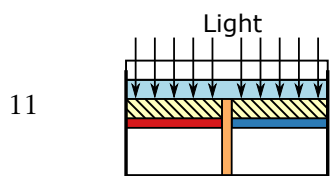
- [137]
- Similar to Design 6 but maximises the ratio of the projected photo-absorber area to the total projected area (*i.e.* 'tucks' the membrane out of the path of light)
 - Improved current density distribution (*cf.* Design 6)



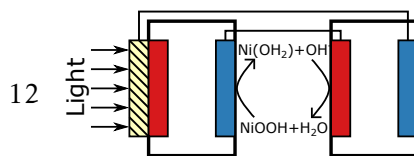
- [149]
- Similarly to Design 8, this improves upon Design 6 by maximising the ratio of the projected photo-absorber area to the total projected area
 - However, potentially large current density distribution issues



- [123]
- Simpler optics for a two separate photo-absorber than Design 4
 - Potential current density distribution issues



- [123]
[150]
- Same advantages as Design 10, plus no light lost due to electrolyte attenuation or reflection at bubbles
 - However, some photo-electrodes are most efficient with front side illumination. Furthermore, if these are PV junction side by side, placing the (dark) electrodes parallel (such as in Design 13) may be more desirable



- [129]
- No current density distribution issues
 - Replaces membrane with solid redox reaction which is periodically reversed to successively charge and discharge the $\text{Ni}(\text{OH})_2/\text{NiO}(\text{OH})$ electrodes

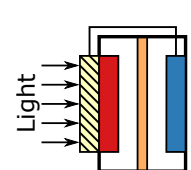
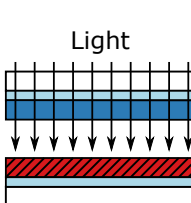
13		• No current density distribution issues • Electrolyte flow may provide temperature control of PV • Not a suitable design for semiconductor-electrolyte junctions
14		• No current density distribution issues and low ohmic losses • Can incorporate photo-electrodes • Product separation requires careful hydrodynamic control • Possible parasitic absorption losses

Table 4.2, whilst not an exhaustive list demonstrates the vast variety of designs reported. In order to assess to what extent does each design meet the engineering requirements for scaling up PEC reactors outlined in Table 4.1, a qualitative ranking system is used for each individual challenge. Table 4.3 displays this assessment, where - denotes an unresolved challenge, o means the challenge was considered but not conclusively resolved, + means the challenge is resolved, and NA indicates this challenge is not applicable to the reactor design.

From this investigation of reactor designs in literature, general trends and observations can be made:

- The STH efficiency achieved is influenced by the reactor design used. For example, the STH efficiency is typically reduced when a membrane is used to separate products or for large area electrodes. This can be observed in the collated data of Ager *et al.* [30], where feasible designs for scaling up (*e.g.* Walczak *et al.* [137]) demonstrate lower efficiencies than small electrode area, high concentration and membrane-less designs.
- For designs employing a membrane, proton-exchange membranes (*e.g.* Nafion®) were common [115, 121, 131]. The rest employed either an anion-exchange membranes (AEM) [146] or a non-ion specific membrane such as a Teflon® diaphragm [121].
- The optical design of the reactors reported can be categorised as:
 1. 'Front side' illumination - Designs 1-3, 4-10, 14

Table 4.3: Qualitative ranking for each challenge in Table 4.1 of selected PEC reactor design where: - = unresolved challenge, o = considered but not conclusively resolved, + = the challenge is resolved, and NA = not applicable. The category of the papers is: t = theoretical, e = experimental, p = patent

Design number	Author	Category	Reference	Substrate conductivity	Electrolyte conductivity	Membrane conductivity	Current density distribution	Window material	Gas evolution	Electrolyte attenuation	pH and conc. gradient	Species cross-over	Limiting mass transfer	Fluid mechanics	Heat management
1	C. Carver 2012	t	[131]	o	+	-	+	o	-	-	+	+	+	+	+
2	T. Lopes 2014	e	[121]	+	+	o	-	o	-	+	+	+	+	-	o
2	Y. Li, 2011	e	[144]	+	+	-	-	o	-	+	+	+	+	+	+
2	M. Graetzel, 2005	p	[145]	-	o	-	-	o	-	-	o	+	NA	-	-
3	A. Hankin 2017	t	[109]	+	+	-	+	o	-	+	+	+	+	-	-
4	T. Lopes 2014	t	[121]	-	+	o	-	o	-	+	+	+	+	-	o
4	Q. Fan, 2007	p	[122]	+	o	-	-	o	-	+	+	+	NA	-	-
5	E. Verlage, 2015	e	[146]	+	+	o	-	o	-	-	+	+	+	-	-
6	E. Selli, 2007	e	[147]	+	+	-	-	o	-	-	-	+	NA	-	-
6	E.L. Miller, 2003	t	[148]	+	o	-	-	o	-	-	o	+	+	+	-
7	S. Haussener, 2012 (b)	t	[123]	+	+	+	+	o	-	-	+	+	+	-	-
7	T. Bosserez, 2016	e	[107]	+	+	NA	+	NA	-	-	+	-	+	-	-
7	F. Bedoya, submitted	t	-	+	+	o	+	o	o	o	+	+	+	-	o
8	K. Walczak, 2015	e	[137]	+	+	o	o	o	-	-	+	+	+	-	o
9	X. Deng, 2010	p	[149]	+	+	-	+	o	+	-	+	+	NA	+	o
10	S. Haussener, 2012 (a)	t	[123]	+	+	+	+	o	-	-	+	+	+	-	-
11	S. Haussener, 2012 (a)	t	[123]	+	+	+	+	o	+	+	+	+	+	-	-
11	B. Turan, 2016	e	[150]	+	+	NA	o	+	+	+	+	-	+	-	-
12	A. Landman, 2017	e	[129]	+	+	NA	+	+	+	+	+	+	+	-	-
13	N Kelly, 2008	e	[151]	+	+	NA	-	-	-	-	+	-	+	-	-
13	J. Becker, 2017	e	[152]	+	+	o	+	+	+	+	+	+	+	+	+
13	S. Tembhurne, 2016	t	[43]	+	+	+	+	NA	+	+	+	+	-	-	+
14	I. Holmes-Gentle, 2017	t	[1]	-	+	NA	+	o	+	+	+	o	+	+	o

2. External (which includes 'backside') illumination - Designs 11-13
3. 'Dual' illumination - Design 4

External illumination has clear superiority in terms of simplicity of optical design.

- For mono-polar configurations that contain a photo-electrochemical interface or a 'buried' PV, there is competition between achieving current density uniformity and ensuring an unobstructed path for the light. For example, Design 1 has the issue that the light is obstructed by both the cathode mesh and the membrane. On the contrary, if the configuration is reversed as in Design 2, the optical path is unobstructed but there is likely now current density distribution issues. This could be solved by adding perforations such as in Design 3, though this could reduce the photo-active area. Design 13 (membrane-less), allows for unobstructed light to 'front side' illuminate the photo-anode but will require a transparent cathode (or semi-transparent photo-cathode).
- For bipolar monolithic designs (Design 6-9), minimising the current density distribution is an intrinsic issue. Therefore, a number of authors have suggested a perforated planar plate [107, 153] or the construction of small (enough) repeating units [123, 137] in order to circumvent this issue. If the dimensions of the repeating units are miniaturisation further (*ca.* μm), one arrives at the membrane-embedded semiconductor microwire design as proposed by Lewis [154, 155]. However, a common drawback of perforations is that photo-active area is lost to membrane area and the 'louvered' design (Design 8) [137] cleverly avoids this by placing the membrane out of the path of the light.
- Only a minority of authors considered the fluid dynamics of the electrolyte in the reactor [1, 121, 131, 137, 144]. It is likely that continuous systems are more suited to scale up and as electrolyte flow can improve mass transfer [114] and facilitate bubble removal [156], investigation of the fluid dynamics for a newly proposed PEC reactor will become an integral part of the design process.
- Many of the PEC designs tackle a particular scaling-up challenge effectively, but none simultaneously meet all the requirements. PEC reactor design constitutes a complex optimisation problem in order to balance reactor performance, cost and operability. Undoubtedly, this analysis demonstrates that the most straightforward system to scale is an external PV + electrolysis as each component can be optimised separately and hence the complexity of scaling up the complete system is significantly less complex. Nevertheless, integrated PEC designs could obtain cost/performance benefits over a complete separated PV + electrolysis.

Whilst wholly approximate, an assessment of the evolution of PEC reactors design can

be made by using the descriptive ranking scale outlined in Table 4.3. If the grading notation is given the following values $+$ = 1, o = 0, $-$ = -1, NA = 0, the summation of the row will give the ‘net number of resolved issues’. The overall trends that can be seen from Figure 4.5 is that since 2010, there has been a large number of reports of scalable reactor designs and that more engineering challenges have been solved and/or considered for any individual reactor design. This qualitative assessment clearly demonstrates progress made and increasing interest in the field of solar water splitting reactor design.

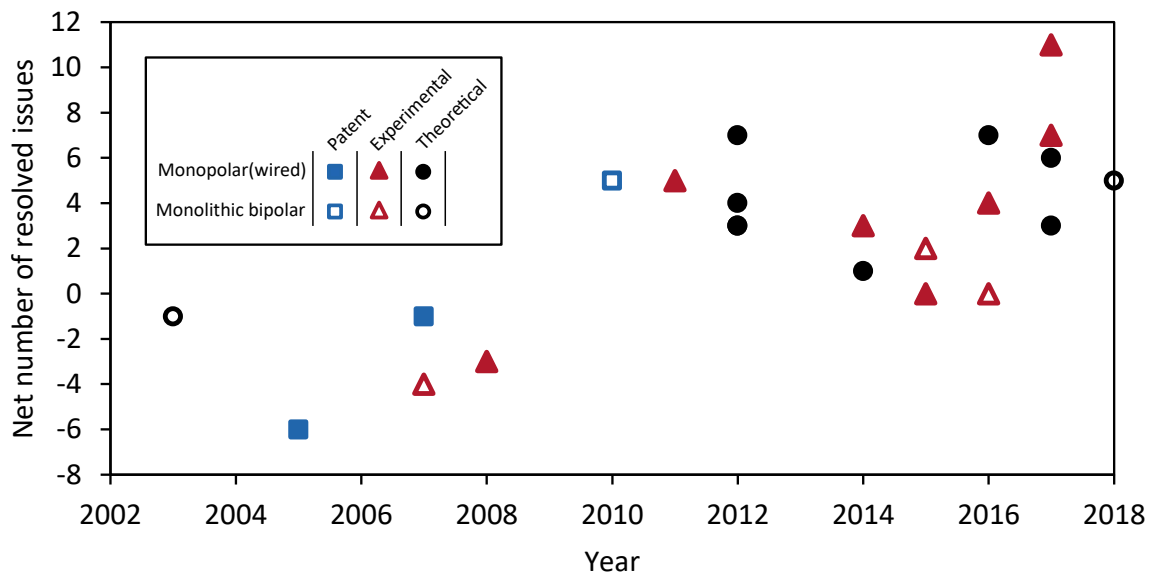


Figure 4.5: The ‘learning curve’ of PEC reactor design. The net number of resolved issues is calculated from the summation of Table 4.3 where $+$, o , $-$ are summed as +1, 0, -1 respectively.

4.5 Conclusions

- The classification framework outlined here is more comprehensive and adaptive than a simple linear progression between a fully integrated PEC to separate PV + electrolysis.
- Designing a scalable PEC reactor is exceptionally more complicated than PV + electrolysis as the design goals are often interrelated and contradictory.
- Progress has been made in the field of scaling up integrated PEC reactors but scalable experimental demonstrations are still scarce.

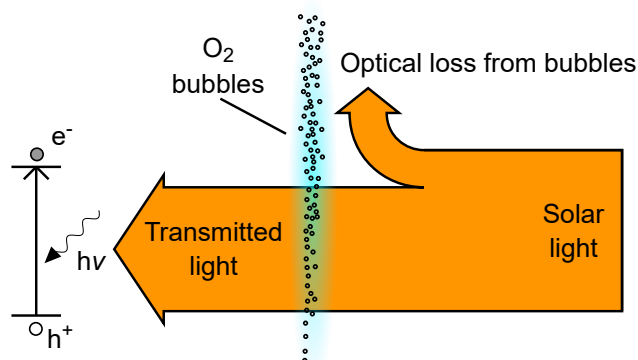
Chapter 5

Optical losses at gas evolving electrodes

Light reflection from the bubbles evolving at the surface of the electrode constitute an energetic loss mechanism. Therefore, an experimental analysis is conducted to assess both the extent of losses and understand the mechanism in order to formulate suitable mitigation strategies for large scale working devices.

This chapter is partially based on the author's submitted publication:

[4] I. Holmes-Gentle *et al.*, "Optical Losses at Gas Evolving Photoelectrodes: Implications for Photoelectrochemical Water Splitting", *The Journal of Physical Chemistry C* **2018**, *123*, 17–28



5.1 Introduction

Reported Solar-To-Hydrogen (STH) efficiencies are now appreciable enough to observe the formation of a significant number of bubbles at the electrochemical interface (*cf.* the videographic supporting information of Goto *et al.* [157]). Some example efficiencies for integrated PEC systems which have a front-side illuminated semiconductor-electrolyte junction include 5.2% [83] and 12.4% [84]. Crucially, in both examples the light must successfully pass through evolving gas bubbles in order to be absorbed at the photo-electrochemical interface. Consequently, the engineering issues involved in gas evolution at photo-electrodes must be quantified and understood in order to design large scale PEC devices and these issues include:

1. Inactive electrode sites due to gas bubble coverage
2. Reduction in the effective electrolyte conductivity as the bubble plume acts as an electrically insulating layer
3. Optical losses due to light reflection at bubble-electrolyte interface

For the first two issues, *i.e.* inactive electrode area and effective conductivity, there has been a comparatively limited amount of discussion and experimental quantification for PEC devices compared to standalone electrolyzers. For example, it is common to see studies where bubble removal is clearly indicated in long time chronoamperometry experiments [146], but studies that explicitly focus on this, such as work by Hernández *et al.* [158], are uncommon. These issues have been studied for dark electrolysis extensively (*e.g.* effect on effective electrolyte conductivity [135, 159] and mass transfer [160]), and the ramifications from these studies should be applicable to PEC systems. This being said, the current densities typically studied in electrolysis ($10^1 - 10^4 \text{ A m}^{-2}$ [161, 162]) are often higher than that in PEC research ($< 60 \text{ A m}^{-2}$ under 1 Sun [163]), which makes the extrapolation of existing models for dark electrolysis to PEC somewhat challenging. Solar concentration of PEC devices could potentially increase the current density to much higher orders magnitude, such as those observed for commercial electrolyzers. In conclusion, there is opportunity for further research into the issues of electrode bubble coverage and increased ohmic losses through the electrolyte, specifically for the low current density bubble evolution regimes typically found in PEC devices.

The third issue, that of light reflection from the phase interface of the gas-liquid mixture, will be the focus of this chapter. Figure 5.1 displays the components of light resulting from the interaction of collimated light with the bubbles. Firstly, light can be transmitted (angle of resulting light $< 90^\circ$ from incident vector), or reflected (angle of resulting light $> 90^\circ$ from incident vector) and both reflected and transmitted light can be further divided into two components: specular or diffuse. Specular means light is

reflected or transmitted in a unidirectional beam whereas diffuse light is scattered at many angles.

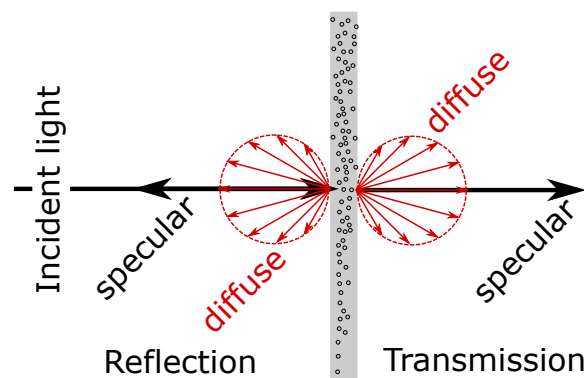


Figure 5.1: Optical components of light scattered from a plume of bubbles

Crucially, if only transmitted light is captured by the photo-absorber and reflected light is lost, bubbles will reduce the ‘optical efficiency’ of the system which will lead to a reduction in the overall achievable efficiency. This energetic loss pathway has been briefly mentioned by a number of authors previously [31, 84, 123, 164–167], with some [164, 167] directly stating that in order to comprehensively model the system, the light lost due to reflection at bubbles must be taken into account. Khaselev and Turner state that 10-20 Suns is a sensible limit, although this is not explicitly referenced or supported by experimental data [84].

Experimental studies investigating the light scattered from bubbles are scarce and thus, the underlying rationale of this chapter is to address this and assess the order of magnitude of typical optical losses and understanding the mechanisms involved. One comparable study by Dorfi *et al.* [168] investigated the photo-current losses from a single hydrogen bubble stuck on the surface and then extrapolated to predict the macroscopic device performance. This ‘bottom up’ approach is in contrast to the ‘top down’ approach outlined in this chapter, where optical losses were determined from average measurements of a population of bubbles. Furthermore, Dorfi *et al.* [168] along with Leenheer and Atwater [169] used Snell’s law and ray tracing to estimate the light path through a single bubble, whereas herein a completely empirical approach is taken. Finally, some studies investigated bubble evolution at the photo-electrochemical interface in order to visualise active sites, as opposed to quantifying the optical losses [170].

This issue of optical losses at gas evolving electrode is all the more pertinent, when optical concentration is considered for PEC devices. Optical concentration may potentially reduce costs [31, 171], but will increase current densities which will consequently increase the number of bubbles formed. The experimental investigation that follows,

is therefore both applicable to the objective of scale up and novel in its assessment of optical losses concurrent with an investigation of the hydrodynamics.

5.2 Experimental section

5.2.1 Design of experimental set-up

The experimental system outlined here aims to measure the amount of light that could be absorbed by the photo-electrode, and therefore the proportion of light that is transmitted through the population of bubbles. This transmitted light contains both diffuse and specular components and the summation of which is called the *hemispherical transmittance*. Therefore, in order to measure as much of the hemispherical transmittance of the plume of bubbles as possible, the detector must ideally capture light scattered at angles up to 90° from incident light vector. Furthermore, in order for the subsequent detection of light transmitted through the bubble film, it must also pass through the gas evolving electrochemical interface to the detector behind. This was facilitated by a transparent electrode made of a thin layer of fluorine doped tin oxide (FTO) deposited on a glass slide.

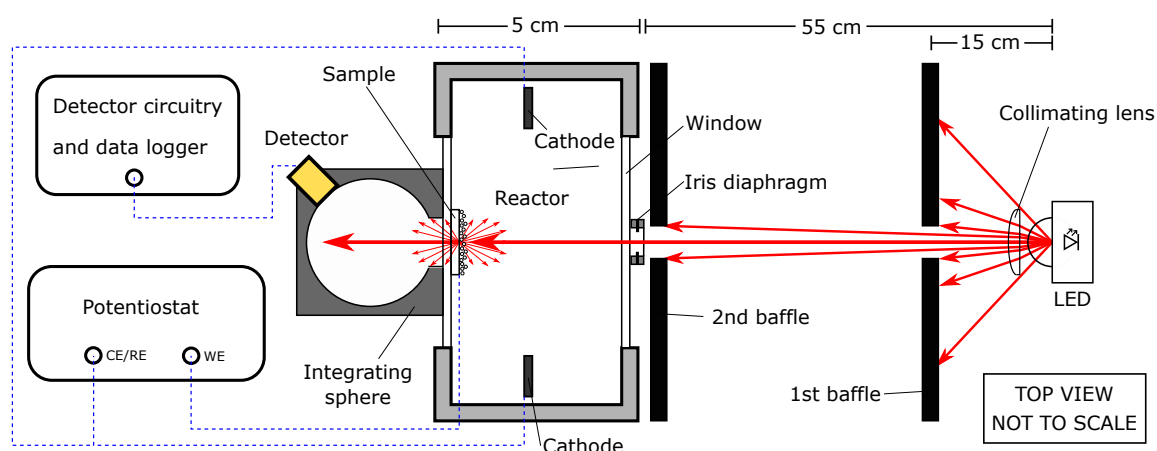


Figure 5.2: Diagram of experimental set-up used to measure the optical losses from a gas evolving electrode ('top down' view)

The experimental set-up is displayed in Figure 5.2, and will be described henceforth in the order of the path of the light (e.g. from right to left in Figure 5.2):

1. Light of wavelength 440-460 nm is produced in a blue LED (LXML-PR02, rebel series, Lumileds) and is focused with a Poly(methyl methacrylate) lens (Lisa2-Pin Real Spot, LEDIL) which has a Full Width Half Max Angle (FWHM) of $\pm 9^\circ$ specified by the manufacturer.

2. Light passes through two optical baffles in order to reduce the stray light received by the detector as this will interfere with the analysis.
3. Light is constrained to circular beam of diameter 10.5 mm by an iris diaphragm.
4. Light enters the reactor through the quartz window and passes through the electrolyte (*ca.* 15 mm path length).
5. Light passes through the oxygen bubbles, if present, evolving at the surface of the transparent electrode. During experimentation, this is the only interface which is changed in the system.
6. If light is successful in passing through the bubbles, it then passes through the transparent electrode (FTO) and out of the reactor through the quartz window at the back
7. Finally, light enters through the aperture ($d = 16$ mm) of an integrating sphere (IC2, StellarNet Inc., Florida). Light is detected at the output port of the integrating sphere using a photo-diode (OPT101P, Texas Instruments Inc.).

The entire experiment was conducted in the dark to minimise interference from stray light, and hence was constructed inside a lab bench cupboard as a dark optical enclosure. Furthermore, a collimating LED lens was used and the sample was placed ~ 60 cm from the light source in an effort to ensure the light is approximately collimated which simplifies the analysis.

An annotated photograph and an ‘exploded’ CAD diagram of the reactor can be seen in Figure 5.3a and 5.3b respectively. The reactor contains the electrochemical environment (*i.e.* electrolyte and electrodes) whilst allowing light to pass in to and out of the reactor through two windows. The reactor was modified from the original design by Carver *et al.* [131], and comprises of PVDF blocks compressed together interspaced with silicone gaskets. The two quartz windows are sealed permanently to the each end of the PVDF frame with silicone sealant. The FTO sample electrodes were fixed to the rear-most quartz window (see Fig. 5.2) with a small quantity of silicone sealant at the corners of the FTO electrode. The counter electrode, in this case a cathode, was positioned in the reactor in order to minimise the current density distribution. This comprised of two identical platinum coated titanium mesh electrodes placed either side of the working electrode (*i.e.* the FTO sample). The reactor was filled with 500 ml of 1 M NaOH (aq.), and this was specifically chosen due to its ubiquitous use as an electrolyte in metal oxide water splitting research. FTO is thermodynamically stable in 1M NaOH at water oxidation potentials [172].

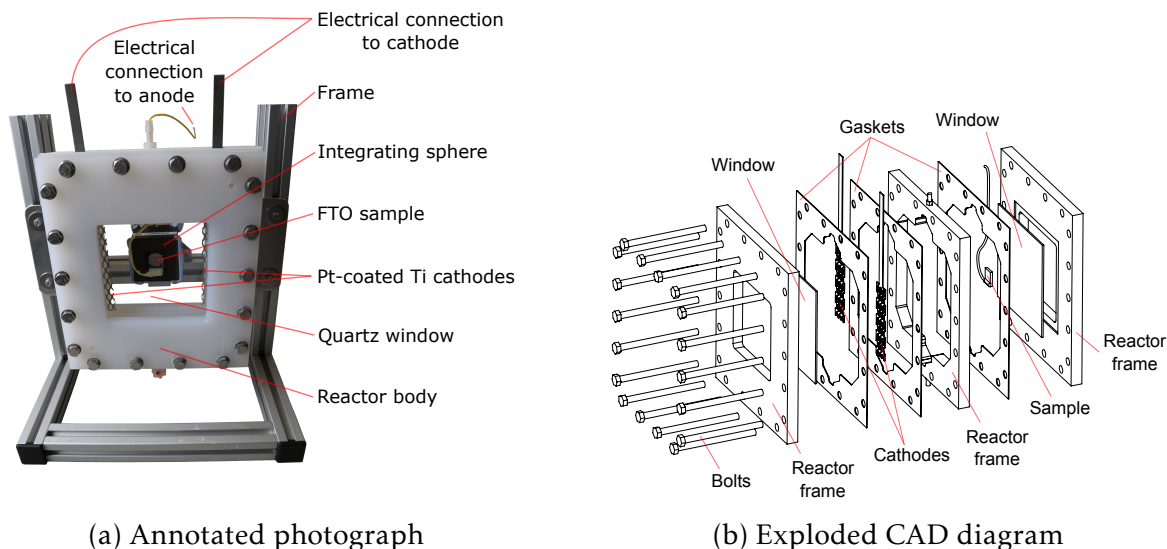


Figure 5.3: Construction of the reactor

A determined attempt was made to ensure that any H_2 bubbles evolved do not interfere with the measurement of O_2 bubbles. In order to stop the bubbles from evolving in the path of the light, the distance between the cathode and sample was maximised. Furthermore, in order to reduce the number of bubbles produced at the cathode and thus reduce H_2 bubble induced convection, a cathode of significantly larger area than the anode was used which helped reduce the cathodic current density.

The electrical connections made to the system are as follows. The working electrode and counter electrode are connected to a potentiostat (1280B, Solartron) in the 'two probe' configuration, that is the counter electrode is used as a reference. The voltage signal from the light detecting photo-diode was logged using a custom made open-hardware potentiostat (DStat [173], more details in Appendix 11.2).

Figure 5.4 shows a more detailed diagram of the FTO sample, highlighting the both the aperture of the light and of the input port of the integrating sphere. The geometric area of the electrode in contact with the electrolyte was 2.25 cm^2 ($1.5 \times 1.5 \text{ cm}$), the diameter of the light beam was 1.05 cm ($A = 0.866 \text{ cm}^2$), and diameter of the integrating sphere input port was 1.6 cm ($A = 2.011 \text{ cm}^2$).

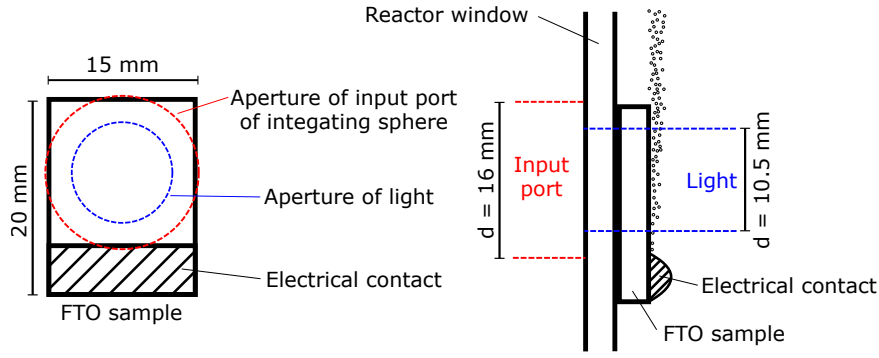


Figure 5.4: Diagram of the FTO sample (front and side view) showing the sampling light beam and integrating sphere input port

Theoretical calculation of the acceptance angle

The majority of light scattered from the bubbles will be captured by the integrating sphere, as shown in Figure 5.5a, and if light is scattered at a higher angle than the critical acceptance angle of the optical system, it will not be measured by the integrating sphere detector. Therefore, in this section an optical *acceptance factor* for the system is theoretically defined closely following the work of Jonsson and Brandén [174].

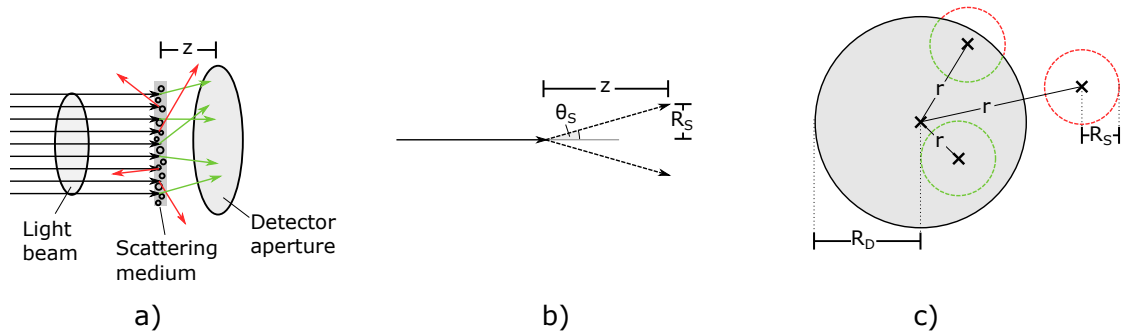


Figure 5.5: Acceptance factor diagrams. The viewers perspective is perpendicular to the incident light vector in a)&b) and parallel in c)

Shown in Fig. 5.5b, if light is scattered at some scattering angle θ_s (measured from incidence), this scattered light at a particular angle will form a *scattering cone* of radius R_s at a given distance from the scattering event z . Next, the incident light travels towards the integrating sphere input port of radius R_D ('D' for detector) and is off the centre of the detector by a distance r . This is shown Fig. 5.5c, where once this off centre light is scattered by θ_s into a cone of radius R_s , it can fall inside the range of the

detector (green circle), outside (red circle), or an intermediate case where only some of the scattered light at a particular angle gets detected (green and red circle).

From this geometric construction, an acceptance factor ψ can now be defined in Eq. (5.1). In short, ψ is equal to one if all the scattered light is detected, 0 if none, and for the intermediate case of partial detection the law of cosines can be used to geometrically determine the fraction of the light detected.

$$\psi(r, R_S, R_D) = \begin{cases} 0 & \text{if } |r - R_S| > R \\ 1 & \text{if } r + R_S < R \\ \frac{1}{\pi} \arccos\left(\frac{R_S^2 + r^2 - R_D^2}{2R_S r}\right) & \text{otherwise} \end{cases} \quad (5.1)$$

Using simple trigonometry, the radius of the scattered light cone R_S can be calculated in Eq. (5.2) from the distance between the scattering event and the detector z and the scattering angle θ_S .

$$R_S(z, \theta_S) = z \tan \theta_S \quad (5.2)$$

Next, if a homogeneous circular beam of collimated incoming light (pre-scattering) of area A_L is considered, an average acceptance factor $\psi_{average}$ can be defined. This is calculated for a particular scattering angle in Eq. (5.3) from the surface integral of the acceptance factor ψ (Eq. (5.1)) divided by A_L .

$$\psi_{average} = \frac{1}{A_L} \iint_S \psi(r, R_S, R_D) dS \quad (5.3)$$

Expressed in polar coordinates for convenience, Eq. (5.3) can be expressed as Eq. (5.4) *via* the substitution of $dS = r dr d\vartheta$ and $A_S = \pi(R_L)^2$ and the assumption that the centre of the light beam and detector coincide. This assumption means that ψ is not dependant on the angular coordinate ϑ , but only on the radial coordinate r and so ϑ can be removed from integral.

$$\psi_{average}(\theta_S) = \frac{1}{\pi(R_L)^2} \int_0^{2\pi} d\vartheta \int_0^{R_L} \psi(r, z \tan \theta_S, R_D) r dr = \frac{2}{(R_L)^2} \int_0^{R_L} \psi(r, z \tan \theta_S, R_D) r dr \quad (5.4)$$

MATLAB was used to solve Eq. (5.4) using the inbuilt numerical integration tools, and the results of this can be found in Figure 5.6. This displays the dependence of average acceptance factor $\psi_{average}$ on the scattering angle θ_S for three different distances between scattering plane and detector z . The minimum value for z will be 6 mm as both the quartz glass and the FTO glass slide are 3 mm thick.

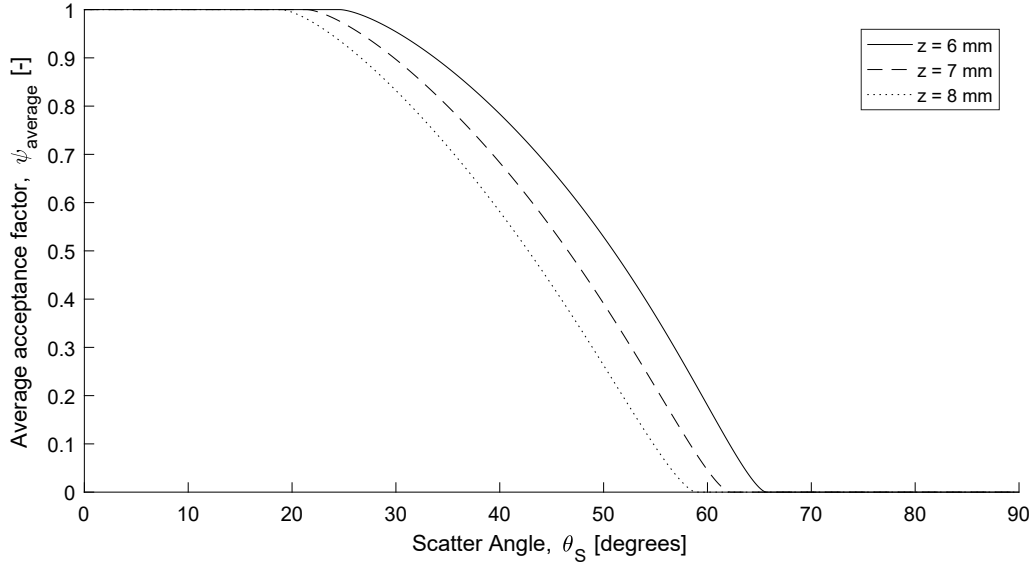


Figure 5.6: Acceptance factor of experimental set-up ($R_D = 16$ mm, $R_L = 10.5$ mm, $z = 6 - 8$ mm,) at a range of scattering angles

Figure 5.6 shows for $z = 6$ mm the majority of scattered light (up to a scatter angle of $\sim 50^\circ$) is captured. Whilst, this demonstrated that this system does not completely measure the hemispherical transmittance, it captures enough of the scattered light in order to assess the scale of this previously understudied issue. Furthermore, the reflectance from the planar semiconductor-electrolyte interface will increase with angle of incidence, which will lead to reduced efficiency at higher angle of incidence light [57]. This effectively means that this un-captured higher angle light ($>50-90^\circ$) may not be captured efficiently, which further justifies the experimental set-up used here. However, there are notable deviations for textured surfaces, such as nanostructured arrays, which have been shown to have a non zero optimal angle of incidence [175].

Optical calibration to ensure linearity of photo-diode

As the linear relationship between light intensity and measured signal is important for the analysis described later, the system was calibrated. This was achieved by placing a number of neutral density filters in the path of the light and measuring the resulting voltage of the photo-diode, the results of which are shown in Figure 5.7. This demonstrates the recorded signal to be highly linear with changes in light intensity. This is as expected as the manufacturers technical notes state that the photo-diode is linear to ± 0.01 % full scale.

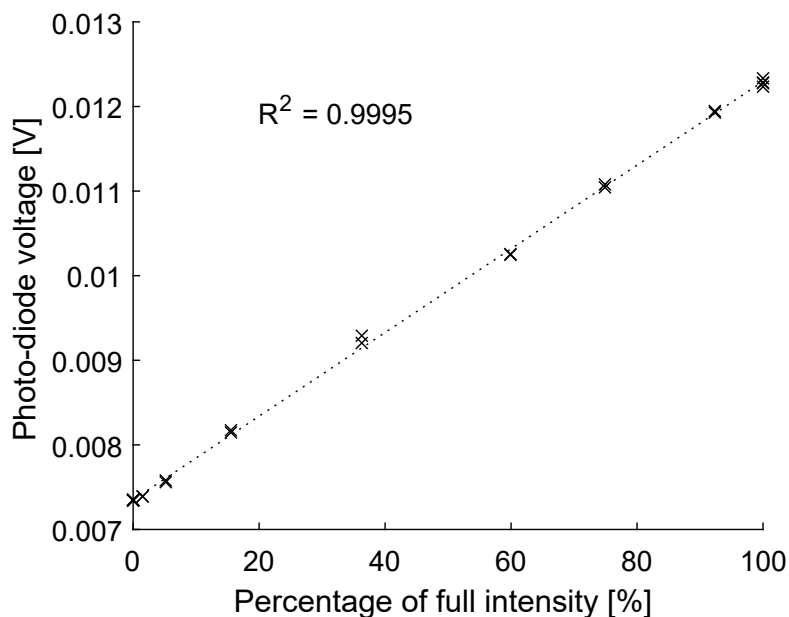


Figure 5.7: Calibration of the optical response of system using neutral density filters

5.2.2 Experimental methodology

Transparent electrode preparation

The FTO was cut to size using a diamond tip glass cutter, and cleaned with successive ultrasonication in acetone and de-ionised water. A PTFE coated wire was electrically connected to the FTO with silver conductive epoxy (CW2400, Chemtronics®) and this connection was subsequently protected from the electrolyte with multiple layers of epoxy. This ensured that the silver epoxy, which is not stable in the electrolyte, does not get oxidised.

Galvanostatic bubble generation

The evolution of bubbles from the surface of FTO sample was controlled galvanostatically, *i.e.* constant current, at 6 different current densities: 0.5, 1, 2, 4, 6, 8 mA cm⁻². The relationship between current density and the resulting bubble evolution regime was observed to be highly dependent on the properties and construction of the epoxy/sample interface.

For example, a common problem would be a bimodal distribution of bubble departure sizes where the majority of bubbles would leave as small regular sized bubbles and a minority would adhere to the epoxy/FTO interface and only detach once coalesced with multiple other bubbles. Even though, these large bubbles depart less frequently, they significantly impact the optical properties of the bubble plume as they drastically

reduce the number of bubbles in front of the sample, and thus the optical loss. This can be clearly seen in the side-by-side comparison in Fig. 5.8.

In order to stabilise the bubble regime to one which was repeatable and consisted of no 'stuck' bubbles it was found that soaking the sample in the electrolyte over a time scale of 1-2 days seemed achieved this. It was speculated that this surface treatment perhaps changes the hydrophobicity of the epoxy. The regime observed in this analysis (see right Fig. 5.8) was characterised by: 1) Negligible 'stuck' bubbles 2) Majority of observable bubbles nucleate at bottom of sample then slide up surface growing in size and bubble rise velocity 3) Very few observable bubbles coalescing in rising bubble plume.

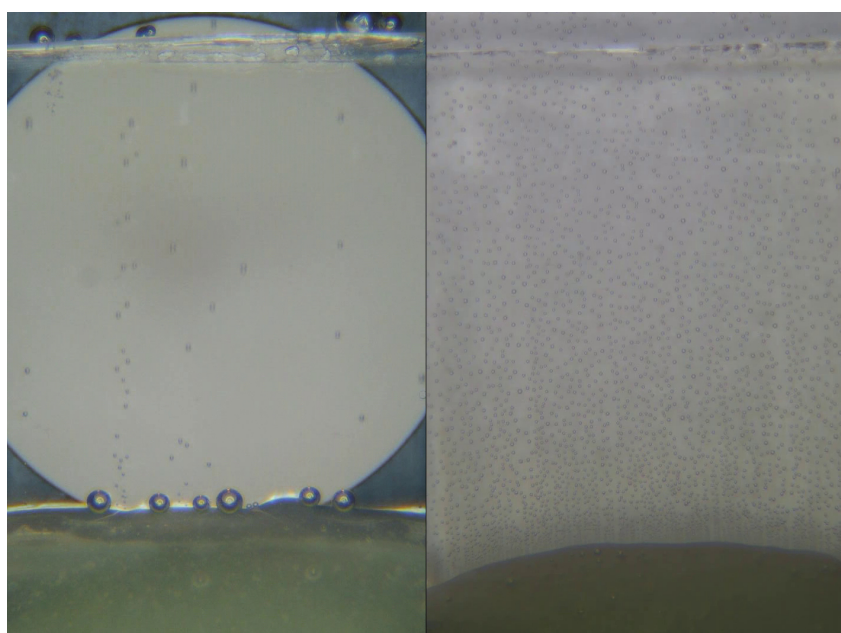


Figure 5.8: Two images of FTO samples at 8 mA cm^{-2} for comparison. Left image: Failed sample where bubbles stick to the epoxy and current 'leaks' to silver oxidation due to incomplete protective epoxy coverage. Right: Sample after surface treatment (1-2 days soaking in 1M NaOH). Note that the left image shows the integrating sphere input port aperture.

It was found that whilst the current density to bubble evolution relationship may vary between samples, the response for any one sample was repeatable. We therefore focus on one sample as a case study in order to investigate the relationship between the bubble plume properties and the optical response, as opposed to the relationship between current density and bubble plume properties.

Measurement of optical losses

The optical losses caused by light scattering from bubbles is measured with the following methodology. Firstly, the LED light source is left to stabilised over 30 minutes in

order for the LED to reach a steady state temperature (as spectrum and intensity are temperature dependent). Then, oxygen bubbles were evolved at the surface of the FTO sample galvanostatically for 3 minutes at a time, interspaced with 1 minute intervals at the open circuit potential so no bubbles were evolved. The bulk electrolyte was not pre-saturated with inert gas but allowed to equilibrate with atmospheric conditions. Over the experiment, the voltage recorded by the photo-diode, and thus the intensity of the transmitted light, is continuously logged.

In order to calculate the optical loss from experimental data taken (*i.e.* the photo-diode voltage), the following theory and assumptions must be invoked. The optical loss is defined as the fraction of total light power that is lost, *i.e.* not transmitted, due to interaction with the bubbles. Assuming the bubble do not absorb any light, and can only be reflected and transmitted then $1 = R_{\text{bubbles}} + T_{\text{bubbles}}$, where R_{bubbles} and T_{bubbles} are the fraction of light reflected from and transmitted through the bubble plume respectively (*i.e.* $R_{\text{bubbles}} = I_{R,\text{bubbles}}/I_o$, $T_{\text{bubbles}} = I_{T,\text{bubbles}}/I_o$). Hence, the optical loss can be expressed as Eq. (5.5).

$$f_{\text{optical loss}} = R_{\text{bubbles}} = 1 - T_{\text{bubbles}} \quad (5.5)$$

The total light transmitted through the bubbles T_{bubbles} can be split into a specular $T_{s,\text{bubbles}}$ and diffuse $T_{d,\text{bubbles}}$ components and related by $T_{\text{bubbles}} = T_{s,\text{bubbles}} + T_{d,\text{bubbles}}$. As previously discussed, our optical system captures all the specular light and the majority of the diffuse light (captured if scatter angle $< \sim 50^\circ$).

The amount of light that is transmitted through the entire optical system, which can be seen in Figure 5.2, will include contributions from other interfaces such as the electrolyte-FTO interface. Therefore, in order to isolate the transmission properties of the bubbles from the irradiance measured by the integrating sphere $I_{T,\text{system}}$, the total transmittance of the bubbles is calculated as $T_{\text{bubbles}}(j) = I_{T,\text{system}}(j)/I_{T,\text{system}}(0)$ where j is the current density applied to the electrode. When zero current density was applied, $j = 0$, no bubbles were generated and the irradiance transmitted is given by $I_{T,\text{system}}(0)$. Next, as shown in the previous section, the irradiance is linearly proportional to the photo-diode voltage. This means the measured irradiance at the output port of the integrating sphere is proportional to the photo-diode voltage with the light source on minus the background voltage in the dark: $I_T \propto \xi_{\text{light}} - \xi_{\text{dark}}$. Finally, the optical loss can be calculated from the raw experimental data with Eq. (5.6).

$$f_{\text{optical loss}}(j) = 1 - T_{\text{bubbles}}(j) = 1 - \frac{I_{T,\text{system}}(j)}{I_{T,\text{system}}(0)} = 1 - \frac{\xi_{\text{light}}(j) - \xi_{\text{dark}}}{\xi_{\text{light}}(0) - \xi_{\text{dark}}} \quad (5.6)$$

An example of a successful experimental run is given in Figure 5.9 following the

experimental protocol outlined in the previous section.

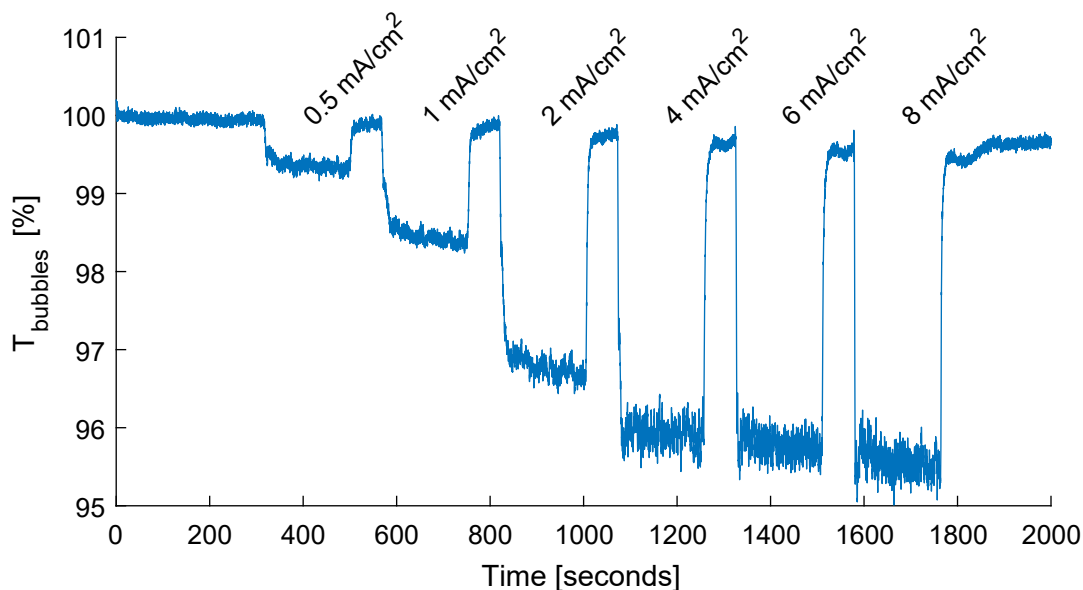


Figure 5.9: Example response from a successful experimental run

Image analysis

A camera designed for the inspection of printed circuit boards (YW2307 ShenZhen YangWang Technology Co., 1280x720 pixels, 30 fps) was used to take 30 images per second of the FTO sample. Video was captured directly after the optical losses measurement as certain components of the experimental set-up blocked the view of the sample (*e.g.* iris diaphragm and optical baffles). The sample was illuminated with an LED microscope ring and the focal point of the camera was adjusted to the plane of the evolving bubbles. Images were taken at two different optical zooms, focused about the centre of sample, where the lower zoom was used to view the entire sample. The higher zoom, which was the highest achievable with the specific microscope camera, is used in order to extract the properties of the bubbles from the images. It was observed that the population of bubbles extended into the solution by less than the depth of field of the optical system, and therefore all bubbles travelling through the field of view were resolved (assuming they are large enough to be seen). If the smallest bubble resolved by the camera is 5 pixels wide, the limit of detection will be a bubble of diameter 16.5 μm .

Care must be taken in ensuring that any artefacts specific to the video set-up are accounted for. In the photographic set-up outlined here, the camera appeared to be returning less than 30 fps (~ 25 fps) whilst the software communication protocol was still attempting to return 30 fps. Therefore the resulting footage contained duplicate frames caused by this mismatch. These duplicate frames were removed and accounted

for in the following analysis by using the fps value that the camera actually achieved (total fps - duplicate fps) in the calculation of bubble rise velocity.

At each current density measured, 5 second of video (150 frames) was taken at the highest zoom and approximately 2 minutes after the start of applying a current in order to ensure the system has reached steady state. These images were subsequently processed and analysed in order to extract key information about the population of bubbles, such as the radius and speed, using a custom MATLAB script. This is published as open source code described in Appendix 11.3 and a screenshot of the Graphical User Interface (GUI) can be found in Figure 5.10. The methodology is outlined henceforth.

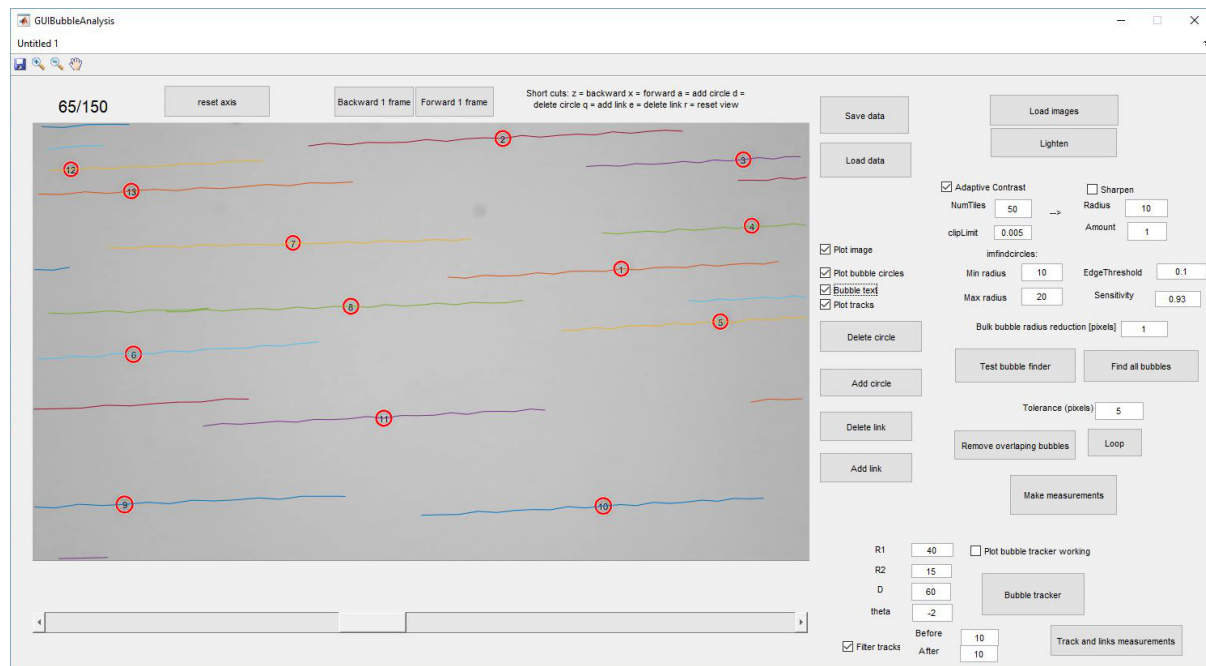


Figure 5.10: Screenshot of the GUI interface of the unidirectional bubble tracker

Firstly, each frame was processed with inbuilt MATLAB functions for adaptive thresholding (*adapthisteq*) and image sharpening (*imsharpen*). The first converts the images to a binary image (each pixel is a 0 or 1 only) and the second step aids the subsequent image analysis.

Then, the location and radius of each bubble in every frame was identified. As the bubbles were spherical, this could be automated using a circle finding algorithm and the inbuilt circular hough transform algorithm was used (*imfindcircles*). The results of the circle detection were manually reviewed and corrected where required. As previously mentioned in literature [176], low shutter speeds can lead to blurring of the bubble images which can distort the calculated radii. Bubble motion blur was observed in the images taken but as the bubble image only blurs in one direction and the bubbles are assumed to be spherical, the circle finding algorithm (utilising circular Hough

transform) appears to calculate radii accurately. This is as the un-blurred dimension limits the calculated bubble size to the actual size.

Next, in order to calculate the speed of the bubbles, the movement of each individual bubble as it passes across the field of view was recorded. Manually tracking each and every bubble over 150 frames would be a laborious task, and so a custom unidirectional bubble tracking algorithm was devised. The method is outlined as follows and is shown in Figure 5.11. The algorithm treats each frame sequentially, looping between first frame to the last. For any given frame (denoted as i), the algorithm loops through each and every detected bubble attempting to locate the same bubble in the next frame (denoted as $i + 1$). This is achieved by constructing a search radius a predicted distance and direction from a bubble in frame i and then determining if any bubbles fall within that search area in frame $i + 1$. The shape of the search area was an ellipse as the bubble velocities varied more than the bubble direction, which helped to ensure that bubbles rising next to one another did not fall into the same search area. Next, the algorithm attempts to link the bubble in frame i to the same bubble in frame $i + 1$ with the following logic. If one bubble is identified within the boundary of the search area a connection is made whereas if no bubbles or 2+ bubbles are found, no connection is made. All these links between bubbles in frames are then compiled into ‘tracks’ which tracks the position of a single bubble over all the frames in which it is visible.

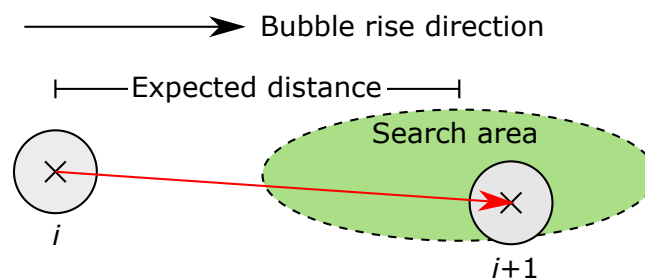


Figure 5.11: Diagram of bubble tracking algorithm showing a single bubble in one frame (i) and the next ($i+1$)

The vast majority of the bubble tracking was successively automated using the unidirectional bubble tracking algorithm, but manual review and correction was still required to ensure accuracy and validity. Careful tuning of the input parameters to the algorithm, such as the expected distance each bubble travels between frames, was found to minimise false positives whilst maximising true positives. It was also found to be preferential to tune the algorithm to not make an incorrect link over omitting correct links, as adding missing links could be corrected manually quicker than correcting errors in the tracks.

5.2.3 The evolution of experimental set-up

The experimental set-up detailed here was the culmination of several preliminary experiments. Firstly, a speculative initial set-up was constructed by shining a laser pointer through an FTO sample and detecting directly with a photo-diode and example data for this can be seen in Figure 5.12. The issue with this preliminary set-up was that only the specular transmission was being detected and the small spot size of the laser, similar to Dynamic Light Scattering, led to a noisy response as a more localised optical loss was being measured.

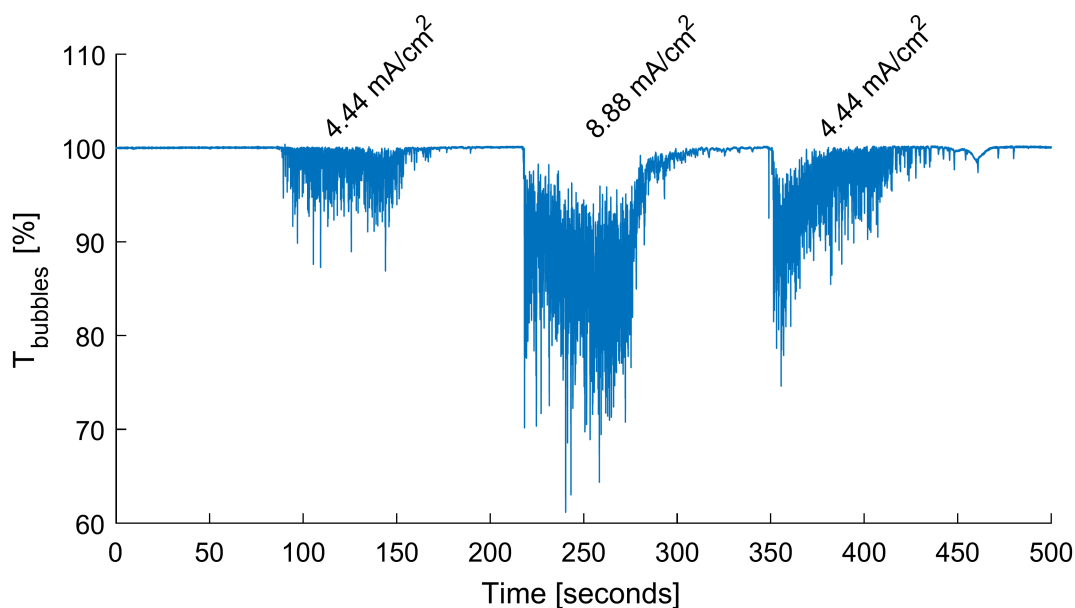


Figure 5.12: Example data from the preliminary optical set-up consisting of a laser and photo-diode

This led to the present set-up, where an integrating sphere is used to capture as much of the transmitted light. The laser was replaced with a LED and the sampling area was increased significantly from the area of the laser spot to the area of light constrained by an iris diaphragm. This facilitated the measurement of the *average* optical loss for a representative sample of bubbles.

The next logical step forward from the analysis outlined in this chapter, would be to construct an experiment that would be able to measure the Bidirectional Transmission Distribution Function (BTDF) of the population of bubbles using an angularly resolved light intensity detector. Theoretically, similar results could be found from varying the distance between the integrating sphere and the sample [174].

5.3 Results and discussion

5.3.1 Measured optical losses

The optical losses from each of the five repetitions was calculated from the raw data and can be found in Table 5.1 for the six current densities applied (0.5, 1, 2, 4, 6, 8 mA cm⁻²). The mean optical loss *vs.* current density is plotted in Figure 5.13 with the error bars displaying plus or minus one standard deviation. It can be seen that at low current densities (0.5-2 mA cm⁻²) the losses increase sharply with current whereas at higher current densities (4-8 mA cm⁻²) the optical losses plateau around ~4.6%. In order to investigate the mechanism behind this response, the properties of the bubble population were analysed.

5.3.2 Analysis of bubble plume

Figure 5.14 shows the location that the images were taken for the subsequent analysis of the population of bubbles. The analysis of the 150 frames (5 seconds) of bubbles evolving at each current was accomplished with procedure outlined in the experimental methodology section and the following properties were extracted: 1) Bubble radius distribution 2) Number of bubbles in a frame (i.e. bubble number density) 3) Velocity distribution of bubbles.

Radius and bubble number density

The mean radius for each current density can be seen in Figure 5.15a and only slightly increases with increasing current density. The histogram of the distribution of the bubble radii shows that the distribution is approximately the same with a slight asymmetrical distribution potentially caused by coalescing bubbles. However, the coalescence of two bubbles was rarely captured in the image. As explained earlier, the position and size of the bubbles in the image was extracted using a circle finding algorithm and this can now be validated as the bubbles observed should be spherical (based on the calculated Reynolds number and Eötvös number) [177].

A more significant change was observed in the average number of bubbles per frame (4.22 × 2.37 mm). This is shown in Figure 5.15b to initially increase with current density and then saturate at current densities similar to when the optical losses (Fig. 5.13) begin to saturate.

Table 5.1: The optical losses of each experimental run for each current densities, along with the calculated mean and standard deviation

Current density [mA cm ⁻²]	Optical loss observed [%]						Mean	SD.
	1	2	3	4	5			
0.0	0.00	0.00	0.00	0.00	0.00		0.00	0.00
0.5	0.81	0.34	0.46	0.46	0.55		0.52	0.18
1.0	2.54	1.65	1.51	1.40	1.54		1.73	0.46
2.0	4.89	3.73	3.38	3.08	3.22		3.66	0.73
4.0	5.12	4.50	4.34	3.89	4.60		4.49	0.45
6.0	4.97	4.31	4.29	4.06	4.82		4.49	0.39
8.0	5.17	4.56	4.40	4.29	5.34		4.75	0.47

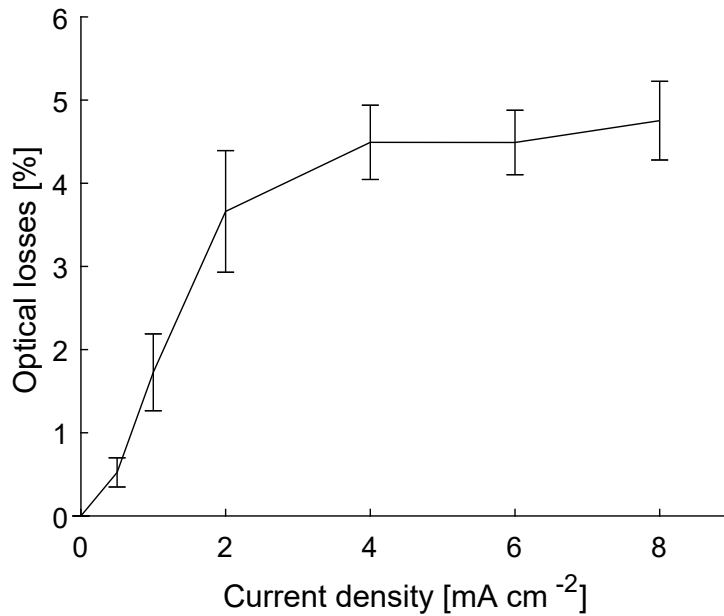


Figure 5.13: Mean optical losses *vs.* the current density applied where error bars show $\pm 1\sigma$ over the 5 experiments

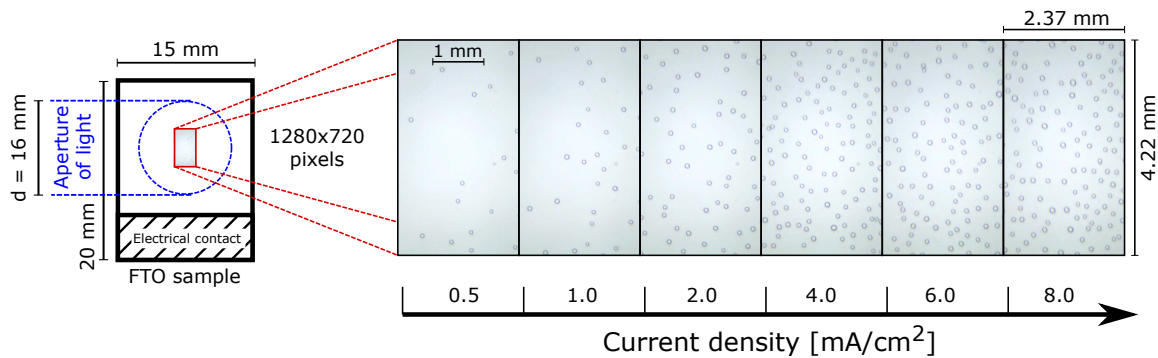


Figure 5.14: Diagram showing the location of video capture and an example image at every current densities applied

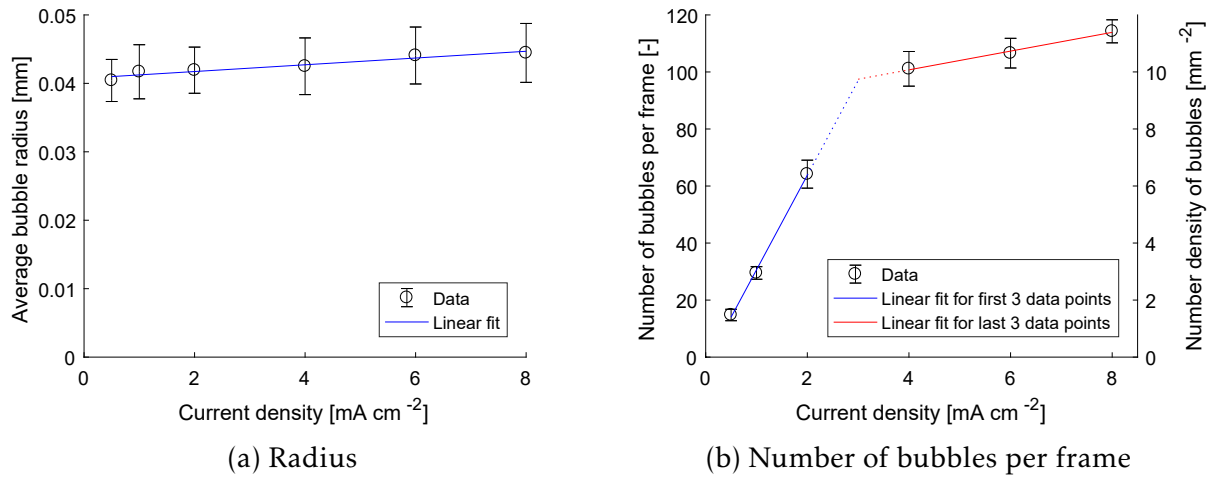


Figure 5.15: Bubble properties *vs.* current density where the error bars denote $\pm 1\sigma$

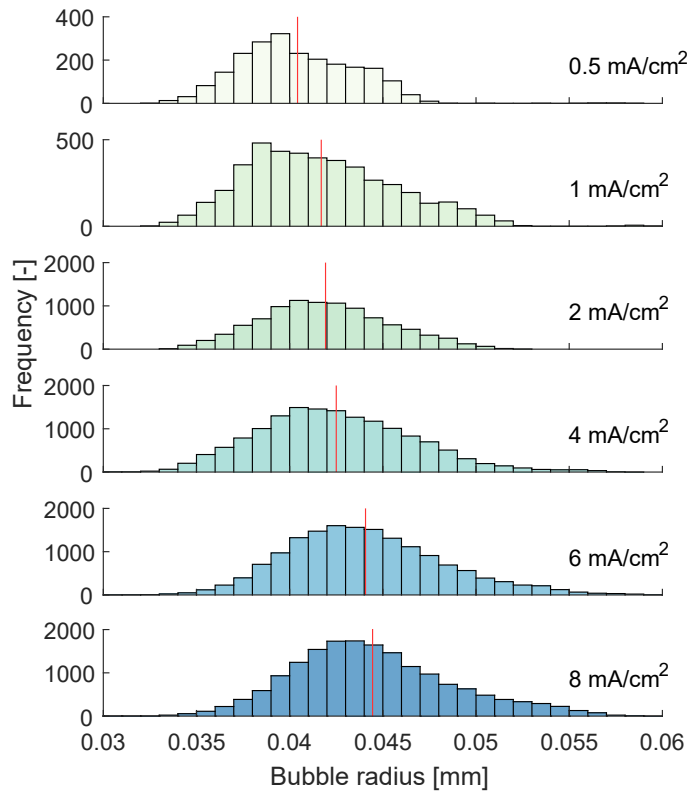


Figure 5.16: Bubble radius distribution over 5 seconds, where the mean is indicated by the red line

Bubble velocity and calculated flowrate

Figure 5.17a shows the mean bubble rise velocity increasing with the current density applied. Whilst the distribution of bubble velocities is quite broad (see velocity histogram in Figure 5.18), the dataset is large (1902 - 13074 points) which means the slight change in gradient between low current densities and high current densities may be significant.

From the bubble radius and the velocities, it is possible to estimate the total flowrate of gas. To begin, the molar amount of O_2 in a single bubble can be estimated with the Laplace equation [169] which accounts for the pressure difference due to surface tension of the spherical bubble surface and the water vapour pressure. This is given in Eq. (5.7) where P_0 is the ambient pressure, P_{H_2O} is the vapour pressure of water in the bubble, γ is the bubble interface surface tension, R is the molar gas constant and T is the ambient temperature. Representative values for these parameters have been taken from literature: $P_0 = 101325$ Pa, $P_{H_2O} = 3344$ Pa, $\gamma = 0.0719$ Pa m, $T = 298.15$ K [178].

$$n_{b,O_2}(R_b) = \frac{(P_0 - P_{H_2O} + 2\gamma/R_b)V_b}{RT} \quad \text{where} \quad V_b = \frac{4}{3}\pi(R_b)^3 \quad (5.7)$$

Since the number of moles in a single bubble of radius R_b can be calculated by Eq. (5.7), the total molar gas flow rate across the area captured in frame can be calculated using Eq. (5.8) where h is the height of the electrode viewed in the frame ($h = 4.22$ mm).

$$\dot{n}_{O_2} = \frac{\langle u_b \rangle \langle N_b \rangle \langle n_{b,O_2} \rangle}{h} \quad (5.8)$$

The calculated molar flowrate of oxygen in observable bubbles flowing across the field of view can be found in Figure 5.17b. This can be compared to the maximum theoretical molar flowrate using Eq. (5.9) given a number of assumptions:

1. All O_2 evolved forms a bubble (*i.e.* the bubble evolution efficiency $f_B = 1$)
2. All current goes to oxidising water (faradaic efficiency $\eta_f = 1$)
3. Current density uniformity over electrode
4. The area responsible for the observed molar flowrate is everything below the centre line of the frame (width = 2.37 mm, height = $15/2 = 7.5$ mm, $A_{below} = 1.78 \times 10^{-5} \text{ m}^2$)

$$\dot{n}_{O_2,theory} = \frac{jA_{below}}{n_e F} \quad (5.9)$$

Now, a comparison can be made between the theoretical molar flowrate and the molar gaseous flowrate calculated from experimental observation (*cf.* Figure 5.17b) and a

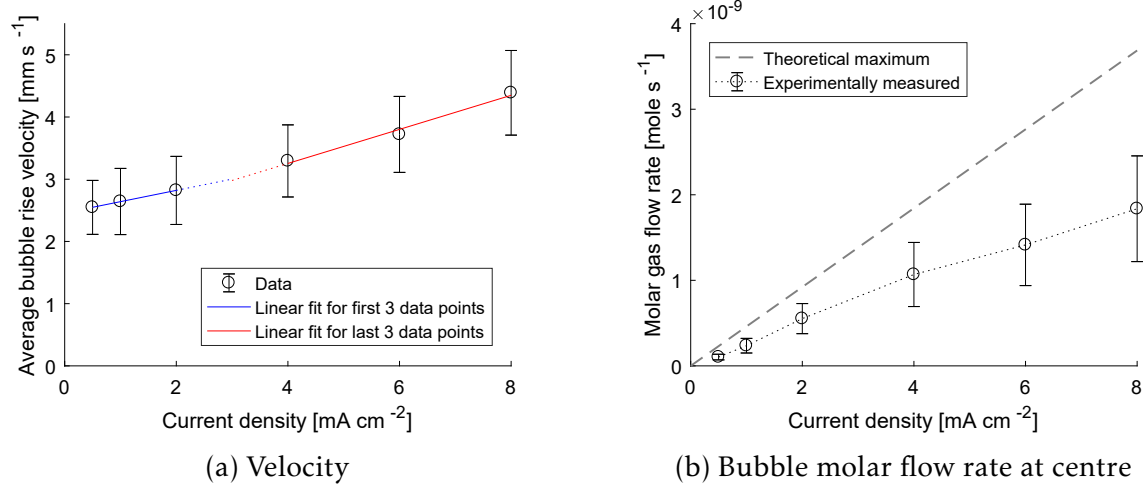


Figure 5.17: Bubble properties *vs.* current density with errors bars denoting $\pm 1\sigma$

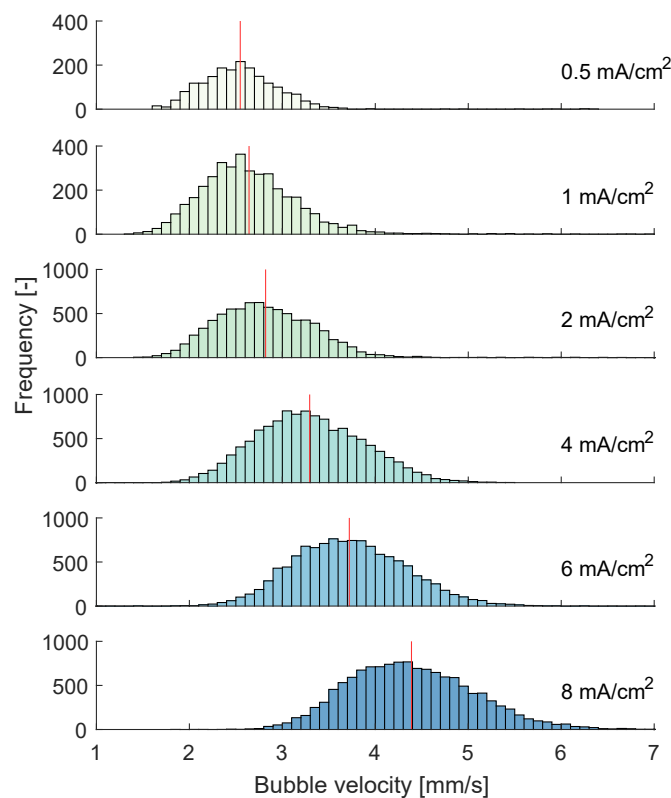


Figure 5.18: Velocity distribution over 5 seconds, where the mean is indicated by the red line

number of key differences are observed. As expected, the observed flowrate is less than the theoretical maximum for all current densities. Furthermore, the fraction that the observed flowrate deviates from the theoretical flowrate, increases at higher current densities. The probable reasons for the observable flowrate deviation will be investigated by a reanalysis of the assumptions made to obtain the theoretical current. Firstly, it is expected that the bubble efficiency f_B which is defined as the fraction of the total molar flux that forms a gaseous bubble [179] will be less than unity [180]. Assuming a faradaic efficiency $\eta_f = 1$, the bubble evolution efficiency f_B can be estimated from the theoretical and observed gaseous molar flowrate with $f_B = \dot{n}_{O_2}/\dot{n}_{O_2,theory}$. This calculated bubble evolution efficiency is plotted *versus* the current density applied in Figure 5.19. Initially, f_B increases with increasing current density, which is expected as increasing the reaction rate at the surface of the electrode should lead to a higher supersaturation in the boundary layer of the electrolyte and hence more O_2 forms a bubble rather than diffusing away. At higher current densities (4–8 mA cm^{-2}), the f_B decreases with increasing current densities. This could be attributed to an increased mass transfer rate due to bubble induced convection [181] and such convection will reduce the local supersaturation at the surface and facilitate the faster removal dissolved gas.

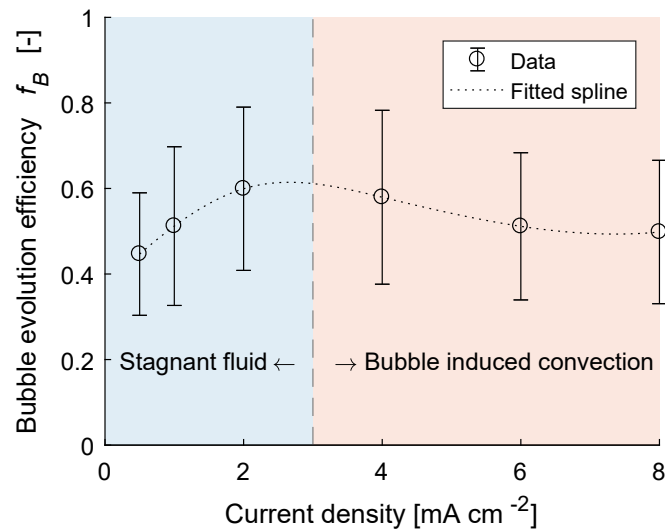


Figure 5.19: Bubble evolution efficiency for various current densities. Error bars show $\pm 1\sigma$

Another assumption is that the faradaic efficiency of water splitting (η_f) was equal to one. This may not be accurate as the reactor does not contain any membrane to stop H_2 being transported to the anode sample and then oxidised, in turn reducing η_f . Therefore, the observed reduction in the bubble evolution efficiency in Fig. 5.19 could be due to an increased mass transport rate of H_2 . Hence, as it stands the hypothesis of the bubble induced convection cannot yet be indisputably confirmed.

Furthermore, throughout this analysis the assumption of a uniform current density over the surface of the electrode is made. As shown in Chapter 6, this may be inaccurate due to the resistance of the substrate FTO, especially for high current densities and large electrode areas. The next section will investigate this assumption in greater detail.

Validity of current uniformity assumption

It is predicted that current density distributions caused by the electrolyte ohmic losses will be minimal in comparison to that caused by the potential drop over the FTO substrate. Therefore, in order to investigate the validity of the current density uniformity, the model outlined in Chapter 6 is used.

The simulation domain was the 1.5×1.5 cm un-masked area and the boundary conditions were electrical connection at the bottom of the electrode and insulating conditions for the left, right and top boundaries. The local current density *vs.* electrode potential relationship was approximated using empirical data for a small area (0.34 cm^2) electrode, and a Tafel was fitted: $j_{anode}[\text{mA cm}^{-2}] = 2.275 \times 10^{-5} \exp(8.421\eta_a)$ where η_a is the anodic overpotential.

The results of the numerical simulation can be seen in Figure 5.20, which show that the higher the average current density, which is what is controlled by the galvanostat, the larger the current density distribution. It follows that, as larger current densities are applied, a larger fraction of the total anodic current flows below the centre of the sample. This is shown in Figure 5.21 and 50.4% and 56.4% of the total current flows below the centre of the sample at 0.5 mA cm^{-2} and 8 mA cm^{-2} respectively.

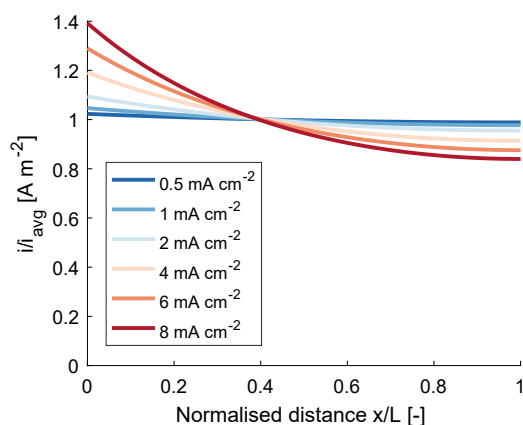


Figure 5.20: Simulated current density distribution from bottom of sample (electrical connection) to top for each average current densities

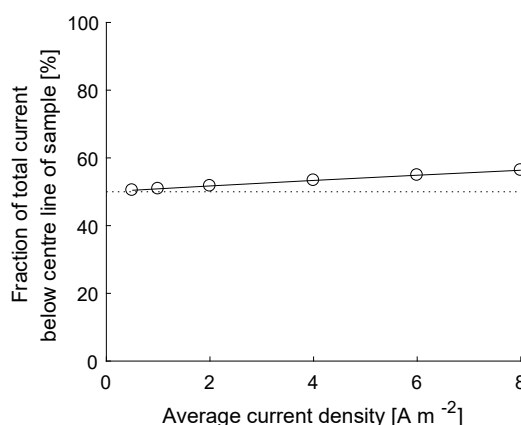


Figure 5.21: Calculated fraction of total anodic current that occurs below centre of sample

Considering only the substrate resistive losses, the expected potential drop over the substrate leads to slightly more O_2 being produced below the centre of the field of view

of the camera. This means the theoretical molar flowrate as calculated by Eq. (5.9) can be corrected for this current inhomogeneity. Figure 5.22 shows that whilst this makes a difference to the calculated bubble efficiency, the overall trends observed stay the same.

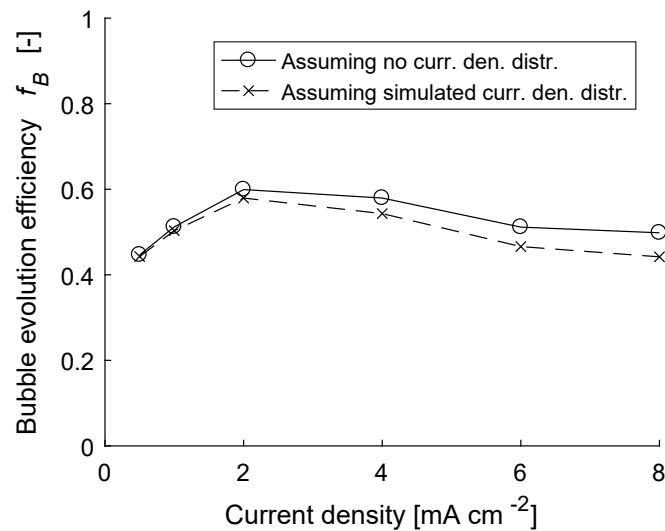


Figure 5.22: Calculated bubble evolution efficiency based on the assumption of current uniformity and based on the simulated current density distribution due to substrate resistive losses

Bubble radius vs. velocity

The rise velocity due to buoyancy forces is dependent on the bubble radius. As many bubbles with a distribution of radii are observed, this can be correlated against the bubbles rise velocity. This relationship is displayed as scatter plots for each current density applied in Figure 5.23.

Stoke's law gives the bubble terminal rise velocity in a stagnant fluid assuming a rigid sphere and $Re \ll 1$ and can be found in Eq. (5.10). Here, u_b is the bubble rise velocity, g is the gravitational acceleration at the surface of the earth, ρ_l and ρ_g the density of the liquid and gas phase respectively, μ_l is the dynamic viscosity of the liquid, and R_b is the bubble radius.

$$u_b = \frac{2g(\rho_g - \rho_l)}{9\mu_l}(R_b)^2 \quad (5.10)$$

The bubble rise velocity in a stagnant fluid of a spherical body that is a fluid, *i.e.* a gas bubble, rather than a solid sphere, is given by the Hadamard-Rybczynski equation (Eq. (5.11)). Here, the rise velocity can be up to $1.5\times$ faster than given by Stoke's law as the fluid bubble cannot support as much tangential stress [182].

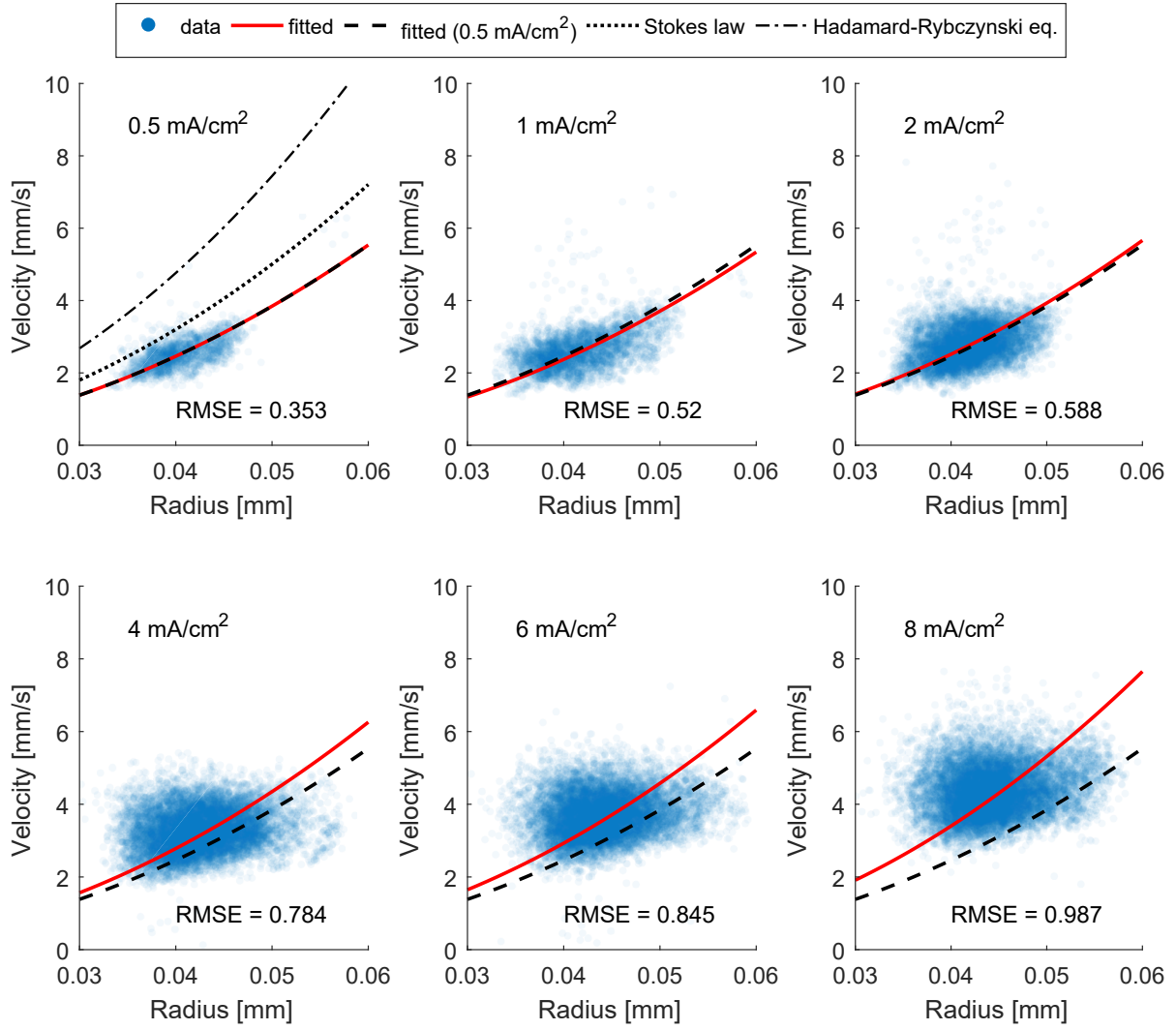


Figure 5.23: The radius *vs.* velocity relationship of bubbles for each of the current densities applied. For each, the fitted curve $u_b \propto (R_b)^2$ is compared to the fitted curve for 0.5 mAcm⁻² demonstrating the increase in velocity at higher current densities. Additionally, the Root-Mean-Square Error (RMSE) increases with current density indicating an increasingly poor fit. Stoke's Law and Hadamard-Rybczynski eq. is shown for comparison with the 0.5 mAcm⁻² data.

$$u_b = \frac{2g(\rho_g - \rho_l)}{3\mu_l} \frac{\mu_l + \mu_g}{2\mu_l + 3\mu_g} (R_b)^2 \quad (5.11)$$

In order to compare the observed data with the theoretical Stoke's law and the Hadamard-Rybczynski equation, typical values were estimated and are given in Table 5.2. In Figure 5.23 the experimental data was fitted to $u_b \propto (R_b)^2$ in order to compare with the theoretical rise velocity in a stagnant fluid.

Table 5.2: Parameters for the theoretical bubble rise models

Name	Symbol	Value	Units	Reference
Liquid dynamic viscosity	μ_l	1.13×10^{-3}	Pa s	[183]
Gas dynamic viscosity	μ_g	2.0459×10^{-5}	Pa s	[97]
Liquid density	ρ_l	1039	kg m ⁻³	[183]
Gas density	ρ_g	1.3088	kg m ⁻³	[97]
Earth's gravitational acceleration	g	9.81	m s ⁻¹	-

The following trends can be seen in Figure 5.23. Firstly, the bubbles move slower than predicted by the Stoke's law or Hadamard-Rybczynski equation. This is perhaps due to the proximity of rising bubbles to the surface of the sample and potentially increased friction and/or due to retardation effects of electrolyte species [182, 184, 185]. In spite of this, the bubbles appear to fit a $u_b \propto (R_b)^2$ relationship well at low current densities. As the current density increases, the goodness of fit indicators such as the Root-Mean-Square Error (RMSE) signal an increasingly tenuous fit. Lastly, the bubbles rise significantly faster for 4 - 8 mA cm⁻² than for 0.5 - 2 mA cm⁻² whilst the mean radius does not increase significantly.

These observations confirm that as the electrolyte is no longer quiescent at the higher current densities which explains the deviation from $u_b \propto (R_b)^2$ to a regime where the velocity is less of a function of radius (*i.e.* induced convection). This concurs with previous observations [136, 186] and discussions [180, 181] that rising bubbles will induce convection at the surface of the electrode increasing the rate of bubble removal and mass transfer.

Consequently, the transition between two flow regimes is observed: Quiescent fluid at low current densities and induced bubble convection at higher current densities. This allows the molar flowrate of gas to continue increasing (*cf.* Fig. 5.17b) whilst the number density of bubbles (*cf.* Fig. 5.15b) plateaus at higher current densities.

5.3.3 Relating optical losses to the bubble evolution regime

It was mentioned earlier that the optical losses (Fig. 5.13) behave in a similar way to the number density of bubbles (Fig. 5.15b). From Figure 5.24, which shows the optical loss *vs.* the number of bubbles in a frame, it can be seen there is an approximately linear relationship between the two variables. This suggests that each bubble scatters a fixed amount of light and that once the light is scattered it is not likely interact with other bubbles (*i.e.* higher order light scattering). At higher current densities than experimentally investigated here, this linear response will likely break down as it will be more probable that the scattered light will interact with other bubbles.

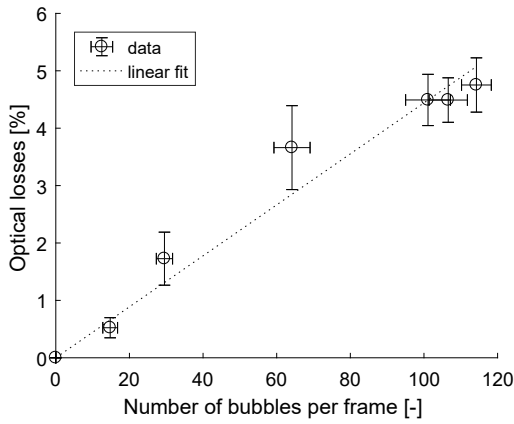


Figure 5.24: Optical losses *vs.* the number of bubbles in a frame

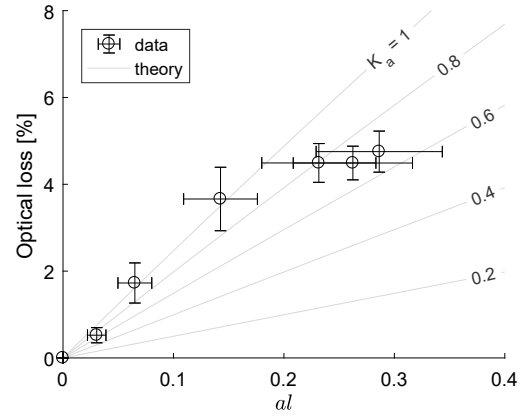


Figure 5.25: Optical losses *vs.* al

The optical scattering can be compared with theory derived for light scattering in poly-disperse liquid-liquid or liquid-gas two phase mixtures [187–191]. It can be derived (see Ref. [187]) that the fraction of light detected, *i.e.* the bubble transmittance T_{bubbles} , is dependant on the dimensionless parameters al and K_a according to Eq. (5.12). Here, a is the interfacial area per unit volume of the dispersion and l is the path length of the light and K_a is the total scattering coefficient explained later. In order to obtain this result, Curl [187] assume that each bubble with a cross-sectional area a_b will have a scattering cross-sectional area a_s where the ratio of the two is the total scattering coefficient K_a . Assuming a collimated beam of light, random position of bubbles, and by neglecting higher order scattering, Eq. (5.12) can be derived from a probabilistic model where a ray of light is only detected if does not intersects with the scattering cross-sectional area of a bubble.

$$T_{\text{bubbles}} = \exp\left(-\frac{K_a al}{4}\right) \quad \text{where} \quad K_a = \frac{a_s}{a_b} \quad (5.12)$$

The optical losses can be related to the bubble transmittance by Eq. (5.5). For the

experimental data taken here, the dimensionless parameter al can be calculated by Eq. (5.13) from the mean number of bubbles per frame $\langle N_b \rangle$, mean surface area of bubbles $\langle A_b^{surface} \rangle$, the height of the frame $h = 4.22$ mm, and the width of the frame $w = 2.37$ mm.

$$al = \frac{\langle N_b \rangle \langle A_b^{surface} \rangle}{hw} \quad (5.13)$$

Figure 5.25 displays the experimental data alongside the theoretical optical loss, for a range of total scattering coefficient K_a values from 0.2 to 1. The experimental results fall within the range $0.6 < K_a < 1$. It is acknowledged that there may be inaccuracies in this analysis caused by the fact that the bubble properties were calculated from the localised image at the centre of the sample (4.22×2.37 mm), whereas the sampling area used to calculate the optical losses is larger (light beam diameter = 16 mm). Nevertheless, this demonstrates that for the sample sizes and current densities described here, an uncomplicated theoretical analysis will give an order of magnitude approximation for the optical losses. This predictive ability will be useful in assessing losses in reactor design and in devising strategies in order to reduce the energy lost due to light scattering at bubbles.

For the experimental range measured here $0 < al < 0.3$, multiple scattering effects are not observed which concurs with literature which suggests that higher order scattering is only significant for approximately $al > 20$ [188, 190]. However, as the theory is derived for specular transmission this critical value of al may be significantly reduced for hemispherical transmittance. Whilst the error in the experimental data taken is quite large, it can be observed that at $al > 0.2$ the experimental data tends towards lower values of K_a , which could potentially be caused by multiple scattering interactions with bubbles.

To the best of our knowledge, this is the first experimental investigation of the optical losses for a population of bubbles evolving from a vertical electrode. Previous work by Dorfi *et al.* [168], investigated optical losses for single H_2 bubbles evolving from a horizontal (with respect to gravity) electrode. They observed an area averaged external quantum efficiency drop of 2.2% to 22.9% for single bubbles of sizes 75 to 500 μm respectively.

5.3.4 Potential future research directions

This study puts an approximate number to the optical losses caused by bubbles. However, it is no way exhaustive and a number of aspects could be investigated in the future:

1. Influence of PEC electrode orientation - Some proposed architectures evolve bubbles from a horizontal electrode [150]; this could lead to larger optical losses as bubbles may spend longer rising in front of the electrode.
2. A more complete theoretical model which takes into account multiple scattering effects could be investigated. This could include ray tracing models with a geometric optical model for bubbles. The optical simulation of very small bubbles would require Mie theory. Simulation of such a large number of bubbles could be computationally challenging.
3. Determine the spectral dependence, if any, of scattering using LEDs of various wavelengths in the visible spectrum.
4. Re-design the experiment in order to angularly resolve the scattered light and measure the Bidirectional Transmission Distribution Function (BTDF).
5. Investigate the predicted optical losses caused by bubbles for different proposed reactor designs (as outlined in Chapter 4).

5.4 Mitigation strategies

When scale up of these devices are considered, it is important to have a knowledge of the optical losses arising from light scattering from bubbles. Photo-electrodes are commonly investigated at the ‘laboratory scale’ with electrode sizes of $< 1 \text{ cm}^2$ which may minimise optical losses due to bubbles and it is predicted that unless careful engineering solutions are employed, losses will be magnified at scale. Therefore, a number of mitigation strategies are investigated.

Evolve fewer larger bubbles

The larger the bubbles, the fewer are required for a given volume of gas. Therefore, for a fixed volumetric flowrate, increasing the bubble diameter will lead to a lower value for al which theoretically will lead to lower optical losses. Unfortunately, this strategies has the significant disadvantage that large bubbles may block the electrode surface and lower effective conductivities. Moreover, Khaselev and Turner actively controlled and reduced bubble size using Triton X-100 in order to mitigate these effects (and corrosion) [84] and Fernández *et al.* used ethylene glycol to modify the properties of evolving H_2 bubbles. It important to note that any additives to the electrolyte such as surfactant must be electrochemically stable and not reduce the faradaic efficiency and both Triton X-100 [193] and ethylene glycol [194] will be likely oxidised at the anode.

Efficient capture of high angle transmitted light

The efficiency of typical planar photo-voltaics and photo-electrodes drops as the angle of incidence increases and so light that has been scattered at a high angle (but still transmitted) may not be efficiently captured. Nano-structured arrays due to their morphology may have a non-zero optimal angle of incidence [175], and this could be potentially exploited to improve the capture of high angle light. However, this would require further study to understand whether this methodology could mitigate optical losses due to bubbles.

Reflect scattered light back onto photo-absorber

If light that is initially reflected from the bubbles is directed back on to the semiconductor, more light could potentially be transmitted through the bubbles and captured. Such a design would have to have small optical aperture through which light enters in order to reduce the amount of light reflected and lost, and the reactor walls would need to be made from a reflective material. This means the interior of the reactor would behave like an integrating sphere. Such a design, with a small acceptance solid angle would likely require optical concentration (to get a large amount of light through a small inlet) and solar tracking, which would increase the balance of system costs. Such an approach could be interesting for particulate systems in a fluidised bed where bubbles would be mixed with electrolyte and photo-catalyst particles.

Remove bubbles faster by increasing convection

As demonstrated in this work, convection increases the rate of bubble removal and therefore optical losses. Rather than rely solely on bubble induced convection, one could force convection by pumping electrolyte through the cell [132]. This could significantly reduce the number of bubbles whilst being simple to implement, though this will require the additional energy input of the pump.

Ensure light does not pass through bubbles to get to photo-absorber

If the charge carriers, *i.e.* electrons and holes, can be excited without passing the light through the bubbles, then the optical losses caused by bubbles can be circumvented. For a photo-electrode, this could be achieved *via* so called backside illumination. It is clear that separated PV + electrolysis will not suffer from optical losses caused by bubbles. If light must pass through the 'front side' to get to the photo-electrode then perhaps better control of bubble formation and release through patterning of catalyst

[195] could ensure bubbles are produced at an optically favourable location, though this may reduce the photo-active area.

An alternative would be to remove the bubbles completely. Such a design could be achieved with dissolved product transported away before supersaturation can occur. The membrane-less design operating at high pressures outlined in Chapter 7 could potentially achieve this.

Direct bubbles behind the electrodes out of the path of light

Inspiration can be found in pre-existing technology from water electrolysis in the form of perforated gas-evolving electrodes. This could be implemented for photo-electrochemical designs in order to achieve the same effect: a reduced number of bubbles in front of the electrode [196]. As shown in Figure 5.26, perforations transport the bubbles behind the electrode *via* bubble induced convection which reduces the negative impact of bubbles (*e.g* a reduction in effective conductivity *etc.*). This will only work for horizontal electrodes, whereas for angled ‘flat plate’ photo-electrodes, forced convection would be required to transport the bubbles behind.

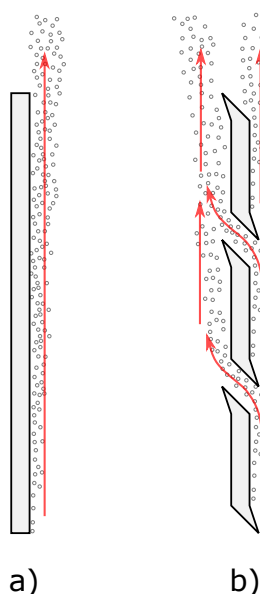


Figure 5.26: Bubble induced convection regimes for a) Planar electrode b) perforated electrode which allows bubbles to be transported behind the electrode

5.5 Conclusions

- Scaled up photo-electrodes operating at the commonly cited 10% STH efficiency target for water splitting [31, 197] will likely suffer from optical losses from light

scattering at the bubbly two-phase mixture. It is highly likely that such designs will require mitigation strategies in order to reduce such losses.

- Losses of up to $\sim 5\%$ was experimentally measured for current densities up to 8 mA cm^{-2} for a sample of FTO ($15 \times 15 \text{ mm}$) and it is demonstrated that the optical losses are highly dependent on the bubble evolution and transport regimes.
- Key parameters of the bubbles such as bubble number density, radius and rise velocity were extracted from video of O_2 evolution from the FTO sample. The optical losses were found to be approximately dependent on the number of optical scatterers, that is bubbles, and both losses and number of bubbles are observed to rise rapidly before plateauing at higher current densities ($> 4 \text{ mA cm}^{-2}$). It is argued that this plateau is caused by increasing bubble induced convection with increasing number of bubbles evolved, which was deduced from the velocity-radius relationship of the bubbles.
- Theory from light scattering in poly-disperse liquid-gas two phase mixtures was compared with the experimental data and found to be similar. Therefore, this study provides an order of magnitude model for use when designing PEC reactors.
- Whilst gas evolution constitutes a significant challenge, these challenges are not insurmountable, with a number of promising mitigation strategies proposed. Notably, from this study one can extrapolate the advantageous effects of forced convection, and suggest a perforated design (inspired by dark electrolysis) that reduces the number of bubbles in front of the electrode and hence reduces optical losses from bubbles.

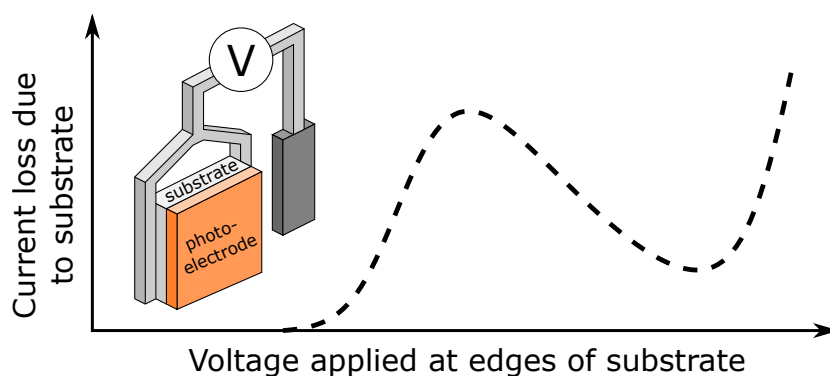
Chapter 6

Modelling resistive losses in transparent conductive oxides

Numerical simulation of the ohmic losses in a transparent conductive oxide substrate permits the critical evaluation of scalability for metal oxide photo-electrode deposited on poorly conductive substrates.

This chapter is partially based on the author's publications:

[2] I. Holmes-Gentle *et al.*, "Assessing the Scalability of Low Conductivity Substrates for Photo-Electrodes *via* Modelling of Resistive Losses", *Physical Chemistry Chemical Physics* **2018**, 20, 12422–12429 - Reproduced with permission from the PCCP Owner Societies.



6.1 Introduction

As shown in Figure 6.1, the electrical conduction path can be grouped into two categories depending on the conduction path within the substrate [106, 198]:

- ‘Wired’ - Electrons are transferred to the substrate from the photo-absorber and the collected at the edges of the substrate. Then, electrons flow to the alternate electrode *via* an external conductive wire
- ‘Wireless’ - Contrary to the wired design, the current is not concentrated, collected at the electrical contact to the substrate and transferred *via* the conductive wire. Electrons can instead flow directly through the substrate to the opposing electrode. A bipolar monolithic stack will often require a ‘wireless’ design.

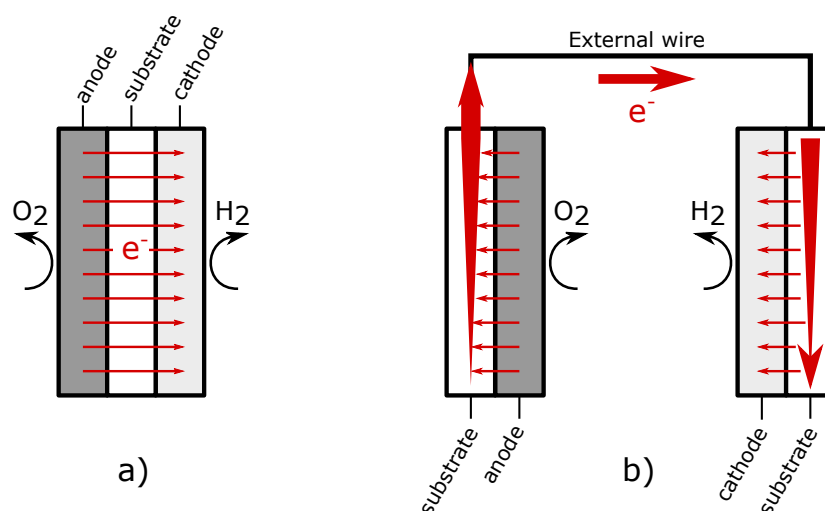


Figure 6.1: Wireless (a) and wired (b) photo-electrochemical device configurations

The electronic conduction path length is likely to be much longer for wired designs compared to wireless designs and therefore the ability of the substrate to conduct charge will be especially important for wired designs. Furthermore, for wired designs, the losses involved in current collection and transfer will be dependent on the electrode areas and so be a function of the extent of scale up. Whereas for wireless designs, as the electrons flow perpendicular to the surface, increasing the geometric electrode area will not change the losses involved in electronic conduction (though will perhaps affect the ionic path length through the electrolyte). Therefore, when investigating the effect of substrate performance on scalability, only wired designs will be investigated.

Presently, whilst many economic studies have focused on wireless designs over wired [31, 199], it is inconclusive which strategy is superior. Furthermore, reduced ohmic losses in the electrolyte and current density uniformity can be achieved more easily

for wired designs intrinsically, without the need for perforations (See Chapter 4) [106, 200]. Additionally, separate electrical connection to each polarity permits additional energy to be supplied (or removed), allows for novel stacked architectures [1, 81], and facilitates half cell diagnostic measurement. Consequently, there is utility in studying the effect of substrate performance in wired designs.

There are a wide variety of substrates used in solar water splitting research. These range from expensive high conductivity substrates, such as gold, to inexpensive lower conductivity substrates, such as transparent conductive oxides. Gold has been used for III-V type photo-electrodes [84], and likewise for mature photo-voltaic technologies driving a separate electrolysis unit, current collection is achieved with highly conductive substrate/busbars typically made of Au or Ag [49, 80, 85].

Transparent Conductive Oxide (TCO) substrates possess a relatively low conductivity (*cf.* the conductivity of copper is typically 100-1000 times higher) but are used extensively with metal oxide photo-electrodes [30, 56]. Examples of TCOs include Fluorine doped or Indium doped Tin Oxide (FTO or ITO respectively). TCOs are often used as a substrate for the photo-anodes due to the ability to form an ohmic junction as the work function of the substrate is likely lower than that of the n-type semiconductor [14, 201], though this is complicated by surface states [202]. For example, the work function of α -Fe₂O₃ and FTO is approximately 5.6 eV [203] and 5.0 eV [204] respectively, therefore one would expect an ohmic contact to be formed between the two materials. Additionally, the transparent nature of TCOs can permit the backside illumination of a photo-electrode, which may potentially be advantageous for some materials [205, 206].

It is important to note that research into the solar water splitting potential of metal oxides is not restrained to TCO substrates, (*e.g.* Fe₂O₃ on Ti [207], WO₃ on W [208], Fe₂O₃ on Fe [209] *etc.*), but the use of transparent conductive oxides is ubiquitous for metal oxide photo-electrodes (*e.g.* Fe₂O₃ [210–212], BiVO₄ [206], TiO₂ [213, 214], WO₃ [215, 216] *etc.*). Therefore, the transparent conductive oxide FTO is chosen as a case study substrate to investigate the resistive losses in the substrate as electrode size is increased from what is conventionally studied.

In order to demonstrate the challenges involved in using TCOs, Figure 6.2 shows ITO being used as the resistive element in an electrical cockpit window heater. Here, electrical energy is being usefully converted to heat, which is the antithesis of the goal when using TCOs as a substrate: ensuring this resistive heating is minimised.

6.1.1 Previous modelling attempts

The impact of substrate conductivity on device performance has been extensively studied for photo-voltaic cells [217–219]. In contrast, there are only two reports



Figure 6.2: Thin-film interference pattern observable on cockpit window due to thin layer of ITO used for electrical heating. ("LHcockpitWindow" by Etan J. Tal is licensed under CC BY-SA 3.0)

(to the best of our knowledge) which specifically tackle this issue for this photo-electrochemical water splitting [131, 133].

Firstly, Carver *et al.* [131] suggested an area of $5 \times 10^{-4} \text{ m}^2$ ($2.2 \times 2.2 \text{ cm}$ square) will result in significant lost current. This work was built upon by Farivar [133], whom also suggested the implementation of gold back contacts in order to circumvent this area restriction. However, the crucial flaw in both models is that they use a Tafel type (exponential) current-potential relationship which deviates from a typical photo-electrode response significantly. This deviation can be seen in Figure 6.3, which shows the current-potential relationship for both the ideal [220, 221] and typical case of a photo-electrode under illumination, for a typical dark photo-electrode, and a Tafel type approximation as made by previous authors. The Tafel type approximation fails to capture the significant behaviour of a photo-electrode such as the deviation from ideal at low potentials due to recombination [140], the photo-current saturation at medium potentials, and the breakdown of the junction (similar to the Zener diode breakdown [141]) at sufficiently high enough potentials.

Consequently, a more advanced analysis than previous modelling attempts is necessary to capture the more realistic performance of a metal oxide photo-electrode deposited on a TCO.

6.2 Substrate resistive 2D model

A mathematical model of the system, is used to simulate the impact of scaling up the photo-electrode area on the current lost to potential drop. This model captures the relevant physics, assumptions, geometry and boundary conditions.

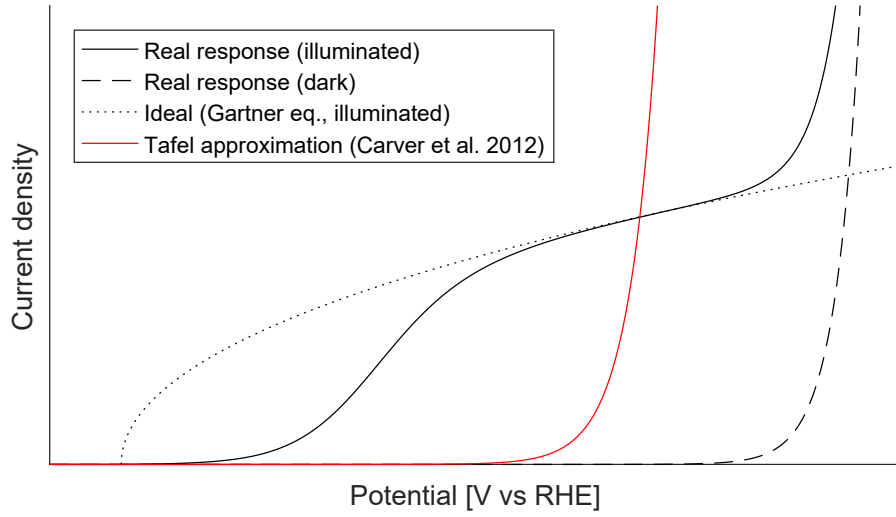


Figure 6.3: Approximate shape of photo-current curve

Firstly, the conduction of electric current within the substrate film in the presence of an electrical field is simulated using Ohm's law in Eq. (6.1) and the continuity of charge in Eq. (6.2). Here, $\mathbf{j}$ is the current density vector, σ the conductivity ($=1/\rho$ where ρ is the resistivity), $\mathbf{E}$ the electric field and Γ_Q is the current sources/sinks within the medium. The electric potential Φ can be related to the electric field $\mathbf{E}$ via $\mathbf{E} = -\nabla\Phi$.

$$\mathbf{j} = \sigma \mathbf{E} \quad (6.1)$$

$$\nabla \cdot \mathbf{j} = \Gamma_Q \quad (6.2)$$

The area of the photo-electrode considered was a square of side length L , and the film width of the substrate is given as L_z .

The following simplifying assumptions reduce the computational complexity of simulation whilst maintaining realism. Firstly, the charge transferred from the photo-absorber to the substrate is treated by assuming that the majority carriers (e.g. electron in a photo-anode) within the semiconductor are transported normal to the surface before transfer across the substrate-semiconductor interface. This assumption is valid as the mean diffusion path length of excited charge carriers is many orders of magnitude smaller than the x, y dimensions of the electrode. For a typical metal oxide, the minority carrier diffusion path length is in the order of nm to μm ($\text{Fe}_2\text{O}_3 = 2\text{-}4 \text{ nm}$ [222, 223], $\text{WO}_3 = 150 \text{ nm}$ [224], $\text{TiO}_2 = 10 \mu\text{m}$ [225]) in comparison to the electrode edge length L of 5 - 50 cm studied here. This assumption negates the need to simulate both the FTO and semiconductor simultaneously. This assumption is summarised in Fig. 6.4.

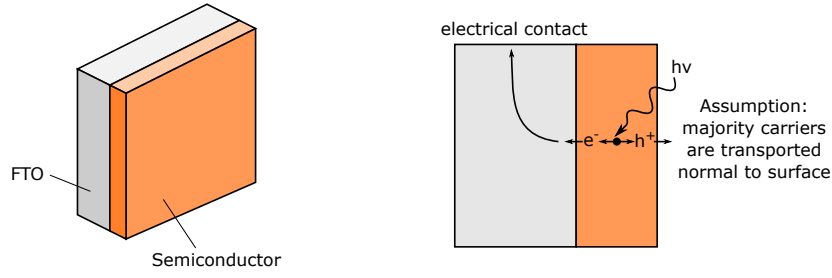


Figure 6.4: Graphic demonstrating the assumption of majority carrier transport normal to the surface

Secondly, the dimensionality of the model was reduced from three to two *via* the removal of the out of plane dimension z . This was achieved by the simplifying assumption that the substrate is sufficiently thin and/or conductive that there is negligible potential drop in the z direction. This assumption is summarised in Fig. 6.5.

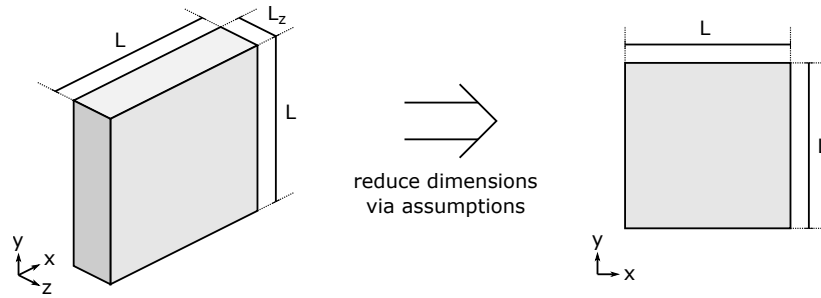


Figure 6.5: Graphic demonstrating reducing the model geometry from 3D to 2D

In order to match the formulation required by the numerical solver, the current source Γ_Q was expressed as Eq. (6.3). Consequently, Eq. (6.1)-(6.2) can be expressed in the form of Poisson's equation as Eq. (6.4).

$$\Gamma_Q = -\frac{j_{anode}}{L_z} \quad (6.3)$$

$$\sigma \nabla^2 \Phi = -\frac{j_{anode}(\Phi)}{L_z} \quad (6.4)$$

The boundary conditions represent the electrical connection to the left and right sides and insulating boundaries top and bottom. Therefore, at the electrical connection the ohmic contact is represented as a Dirichlet boundary condition, $\Phi = \Phi_o$, where the electrical potential is set at some absolute potential (which can be related to an electrode potential E_o at the edge). Insulating boundary conditions are attained by fixing the current density $\mathbf{j}$ normal to the surface (normal vector $\mathbf{n}$) to zero, *i.e.* $\mathbf{n} \cdot \mathbf{j} = 0$. The anodic current (positive if oxidation, negative if reduction) crossing the substrate-semiconductor interface per unit area of electrode due to the electrochemical reaction

at the surface is denoted by j_{anode} and is a function of the electrode potential E at that location: $j_{anode} = f(E)$. Here, the electrode potential can be expressed as $E = \Phi - \Phi_{electrolyte} + constant$ where Φ is potential of the substrate, $\Phi_{electrolyte}$ the potential of the electrolyte and the constant is related to the arbitrary reference electrode system used.

Both previous modelling attempts [131, 133] used a Butler-Volmer relationship as given in Eq. (6.5). However, as mentioned in the introduction, this approach may not be physically accurate for photo-electrode systems.

$$j(E) = j_o \left(e^{\alpha_a f(E-E_{eq})} - e^{-\alpha_c f(E-E_{eq})} \right) \quad (6.5)$$

A better approximation would be one that captures the behaviour of the semiconductor-electrolyte junction such as the analytical equations proposed by Gärtner [220] and Reichman [221]. Since its conception, many authors have discussed, modified and proposed new analytical current-potential for semiconductor-electrolyte interfaces [226, 227] and one notable example from colleagues at Imperial College London multiplied an empirically derived non-ideality factor, which captures captures the recombination effects, with the ‘Gärtner’ equation to give an analytical equation which better approximated experimental data [109]. A numerical solution of the charge carrier drift diffusion equation may also model the photo-current response accurately [228–230]. However, these methods of modelling the photo-electrode current-potential response are complex and may not fully capture non-idealities and therefore empirical data for j_{anode} was used.

A continuous and smooth representation of the empirical data points is advantageous to reduce the repeated interpolation by the numerical solver and avoid numerical inaccuracies. Therefore, the experimental data was fitted to Eq. (6.6) which can be split into two parts. Firstly, the photo-current j_{photo} was represented by a 5-point logistic equation in Eq. (6.7) and secondly, the dark current j_{dark} was represented by a Tafel equation in Eq. (6.8). This formulation was chosen (as an alternative to splines *etc.*) in order to obtain an excellent fit and has the additional advantageous feature that the current-potential response could be extrapolated to different solar intensities through the scaling of j_{photo} in Eq. (6.6). This assumes that the photo-current scales linearly with solar concentration which for metal oxides is likely to be a valid approximation for low intensities (<25 suns) [231, 232].

$$j_{anode} = \frac{S}{S_o} j_{photo} + j_{dark} \quad (6.6)$$

$$j_{photo} = A + \frac{B - A}{\left(1 + \left(\frac{E}{C}\right)^D\right)^E} \quad (6.7)$$

$$j_{dark} = Fe^{G(E-1.23)} \quad (6.8)$$

In order for experimental results to be a valid representation of the local anodic current density j_{anode} , the electrode size of the experimental set-up must be small enough to ensure current density uniformity. Even if this assumption proves not accurate, the energetic losses due to substrate performance could potentially be higher and hence this analysis constitutes a best case scenario.

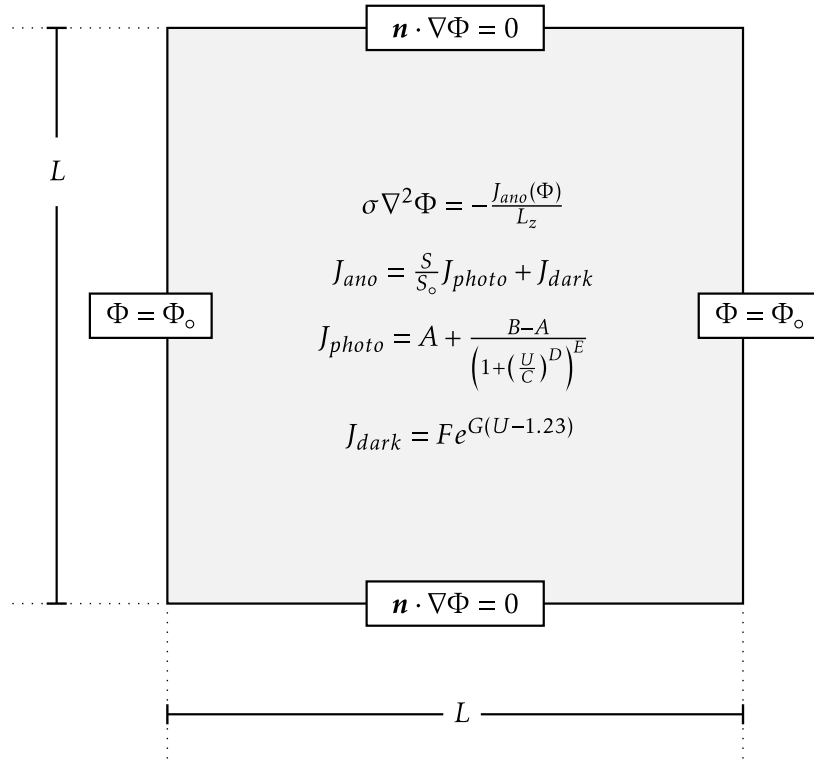


Figure 6.6: Diagram of geometry with model equations and boundary conditions overlaid

Figure 6.6 gives a graphical summary of the model showing the equations solved for, the geometry and the boundary conditions. Finally, this model is intentionally not a complete description of a fully functional device so as to extract only the influence of the substrate performance without considering other physical phenomena such as light inhomogeneity, fluid mechanics or electrolyte current density distribution. Whilst the consideration of electrolyte current density distribution has been shown to be crucial

in PEC systems [109, 131, 167], it is neglected here for the aforementioned reason and hence, $\Phi_{electrolyte}$ is a constant at all locations (for simplicity: $\Phi_{electrolyte} = 0$).

6.3 Model parameters and numerical solution

Numerical solution for Φ was accomplished with COMSOL Multiphysics 5.3 using the inbuilt physical models (*i.e.* stationary electric currents model in the AC/DC module). The input and solver parameters used are outlined in Table 6.1, and a mesh and solver tolerance sensitivity analysis was conducted to ensure the accuracy of the numerical results.

At this point, the substrate selected for study is F-doped SnO_2 (FTO) due to its commonly reported use in water splitting studies and so the results can be directly compared with previous studies. The 2D model, however, is non specific to substrate type as long as the assumptions detailed previously are accurate. By taking the bulk resistivity of FTO ($\rho = 2.2 \times 10^{-6} \Omega \text{ m}$ [233]), and the square resistance of state of the art Pilkington/NSG TECTM product range ($\sim 8 \Omega \text{ sq}^{-1}$), an substrate thickness L_z of $\sim 300 \text{ nm}$ was approximated.

Table 6.1: Input and solver parameters

Physical property	Symbol	Value	Units
Bulk resistivity*	ρ	2.2×10^{-6}	$\Omega \text{ m}$
Substrate thickness	L_z	300	nm
Boundary electrode potential	E_o	0.43-1.66	V <i>vs.</i> RHE
Electrode width and height	L	5-50	cm
Mesh Spacing	$\Delta x, \Delta y$	0.001	m
Solver		Newton Raphson	
Error Tolerance		1×10^{-6}	

* Data source [233]

Several different metal oxide materials were considered and exemplary data was taken from literature for $\alpha\text{-Fe}_2\text{O}_3$, WO_3 and BiVO_4 [81, 102, 210, 211]. The current density *vs.* potential relationship of each photo-electrode was extracted from cyclic voltammetry (CV) plots using Webplot digitizer software [234], and fitted to Eq. (6.6) using a non-linear least-squares solver (*lsqcurvefit* in MATLAB). The fitted parameters for the four examples used can be seen in Table 6.2, where the datasets are henceforth referred to by the first author's last name and date of study (*i.e.* Tilley2010, Kim2013, Brillet2012 and Kim2016).

Whilst four experimental examples of three different metal oxides deposited on FTO are simulated, we will focus on the Tilley2010 dataset ($\alpha\text{-Fe}_2\text{O}_3$) as the larger experimental

potential window allows more of the dark current to be observed. The range of potentials studied in the Brillet2012 (WO_3) and Kim2016 (BiVO_4) datasets are such that the dark current is not observable and so Eq. (6.8) was manually set to zero (by enforcing $F = 0$).

Table 6.2: Fitted current response parameters

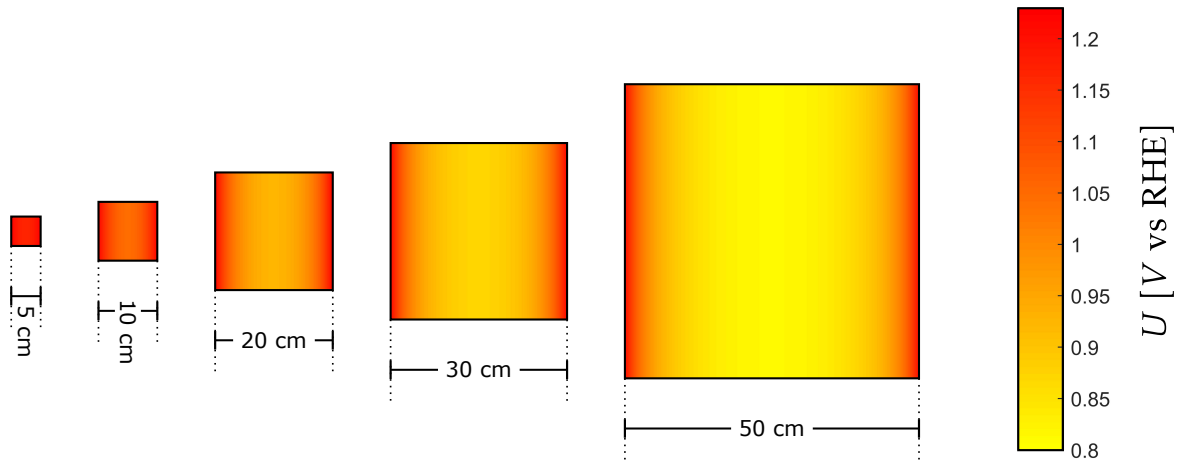
		Dataset name			
Parameter	Units	Tilley2010 [211]	Kim2013 [210]	Brillet2012 [102]	Kim2016 [81]
Material	-	Fe_2O_3	Fe_2O_3	WO_3	BiVO_4
A	A m^{-2}	38.7	124.3	25.9	57.8
B	A m^{-2}	0.00	0.00	0.00	0.00
C	V	0.981	0.642	0.645	0.355
D	-	17.1	27.0	8.90	5.75
E	-	0.421	0.0414	0.522	0.271
F	A m^{-2}	0.00507	1.22	0.00	0.00
G	V^{-1}	17.0	27.9	0.00	0.00
Minimum	V	0.799	0.424	0.517	0.245
Maximum	V	1.66	1.27	1.46	0.940

This analysis was carried out with multiple metal oxide materials in order to demonstrate issues surrounding scalability of TCOs are not specific to the semiconductor material used. Furthermore, any higher efficiency material than investigated here will incur higher resistive losses.

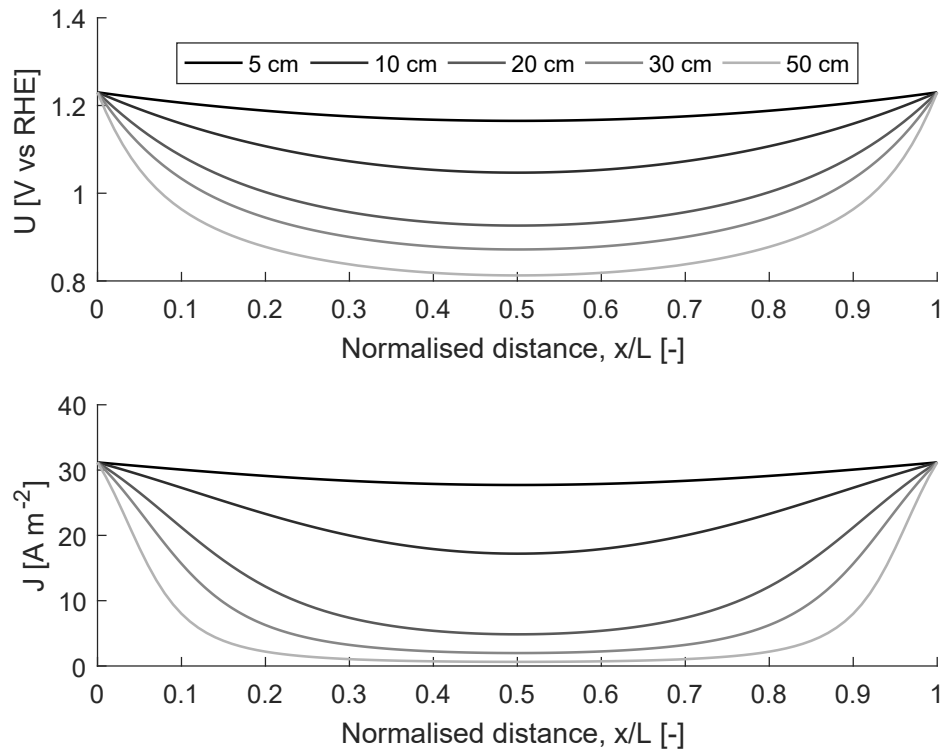
6.4 Simulation results

An electrode potential (relative to RHE) distribution is formed within the conductive substrate and Figure 6.7a demonstrates this for different electrode sizes. An edge electrode potential of 1.23 V *vs.* RHE has been chosen as it is the typical operation point for benchmarking the performance of oxygen evolving photo-anodes. This clearly demonstrates that the larger the electrode, the greater the loss of electrical potential toward the centre. Figure 6.7b, shows both the voltage and the current density distribution for a ‘cut line’ across the sample from $x = 0$ to L for various electrode sizes. For the large area photo-electrodes, it can be seen that this voltage drop results in a significantly inactive region around $x/L = 0.5$ characterised by low current densities.

The average (mean) current density $\langle j \rangle$ was calculated *via* Eq. (6.9) at every boundary electrode potential E_o simulated. This is achieved by dividing the surface integral of



(a) Colour map diagram of the substrate electrode potential for when the electrical contact boundary condition is $E_o = 1.23$ V *vs.* RHE



(b) Potential distribution at $y = L/2$ for a boundary condition $E_o = 1.23$ V *vs.* RHE for various electrode sizes

Figure 6.7: Potential and current density distribution across substrate for the Tilley2010 dataset (Fe_2O_3)

the local current density by the total area of the surface of the photo-electrode A_{PE} .

$$\langle j \rangle(E_o) = \frac{\iint j(E) dx dy}{A_{PE}} \quad (6.9)$$

Then, the average current density can be compared with the current density of the infinitely small electrode which not be affected by substrate performance. As $L \rightarrow 0$, the average current density $\langle j \rangle(E_o) \rightarrow j(E)$. This comparison of the average current density can be seen in Figure 6.8, which clearly shows the reduction in current as the edge length L increases. When the gradient of local current density $j(E)$ with electrode potential E is high, then a small drop in potential due to ohmic losses will cause significant respective current loss. Therefore, it can be observed in Figure 6.8 that steep sections get ‘smoothed out’ through operation at higher current density.

This total current density lost when compared to an infinitely small electrode can be defined by Eq. (6.10) and is shown for each dataset considered in Figure 6.9. The current loss due to substrate performance initially increases with increasing edge electrode potential E_o , before reducing as the photo-current plateaus. Finally, for the datasets where the dark current is observable (Tilley2010, Kim2013), the current losses begin rising again at potentials where the dark current is observable. It should be noted that this behaviour will not be seen in previous studies that used Butler-Volmer/Tafel type relation to describe the photo-electrode kinetics [131, 133].

$$\text{Fraction of current lost to substrate resistance} = \frac{j - \langle j \rangle}{j} \quad (6.10)$$

The general trend is similar for all datasets but some display a greater difference between the minima and maxima in the loss current lost. The flatter the photo-current saturation region (at higher potentials before junction break down is observable), the lower the minima. Consequently, the ratio of the minima to maxima is highest for the Kim2013 dataset, which exhibits the steepest photo-saturation region before dark current.

6.4.1 Effect of solar concentration

As solar concentration may reduce total device costs [31, 110], the effect of solar concentration on the current lost due to substrate resistivity was investigated. The performance of the photo-electrode can be extrapolated for greater numbers of Suns (using Eq. (6.6)) which assumes that the photo-current scales linearly with light intensity. This is typically the case [14] and has been shown to be valid for hematite up to 25 Suns [232]. Furthermore, in order to simulate the system, device temperature

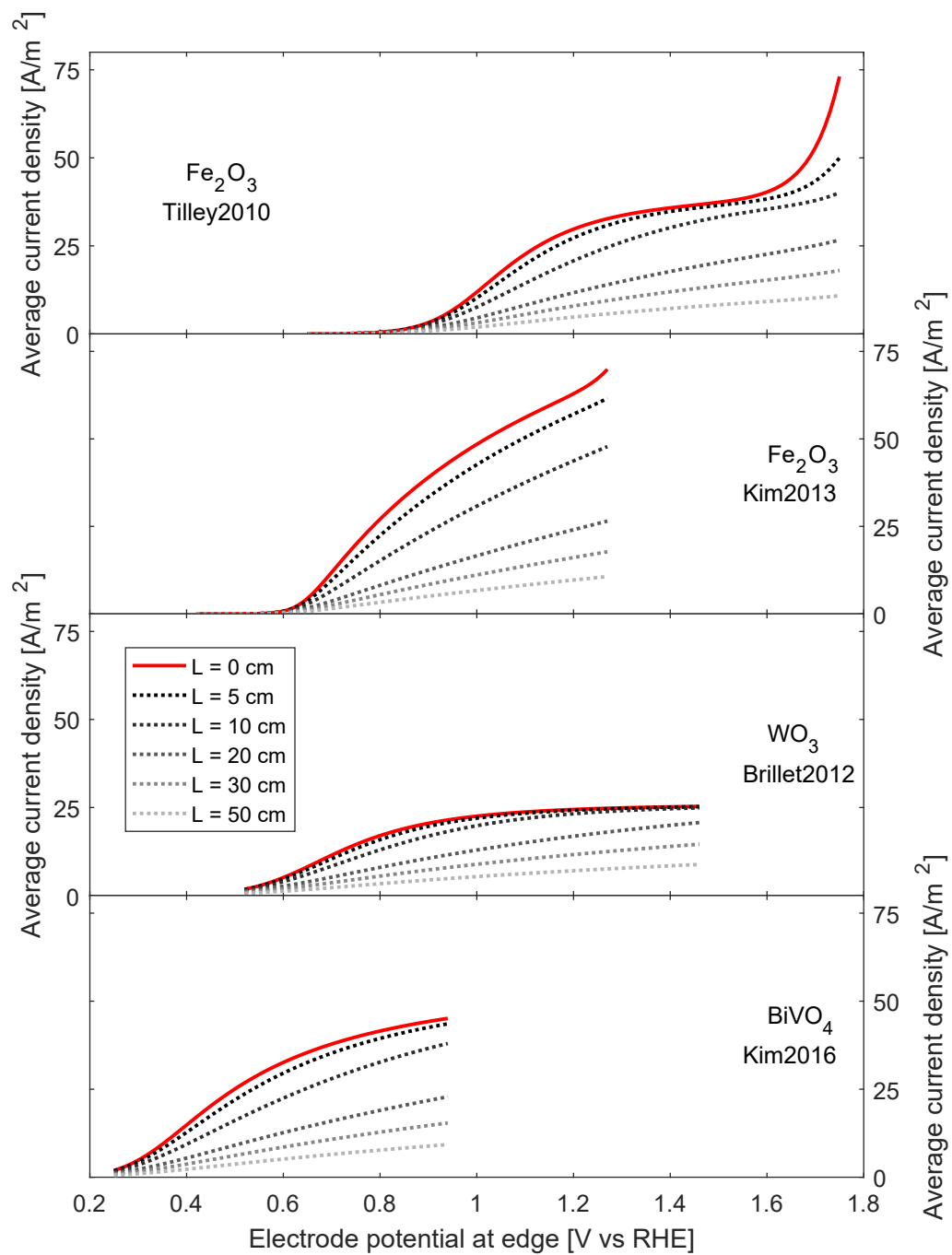


Figure 6.8: Mean current density for various electrode sizes using Tilley2010 (Fe_2O_3), Kim2013 (Fe_2O_3), Brillet2012 (WO_3) and Kim2016 (BiVO_4) datasets compared to an infinitely small photo-electrode

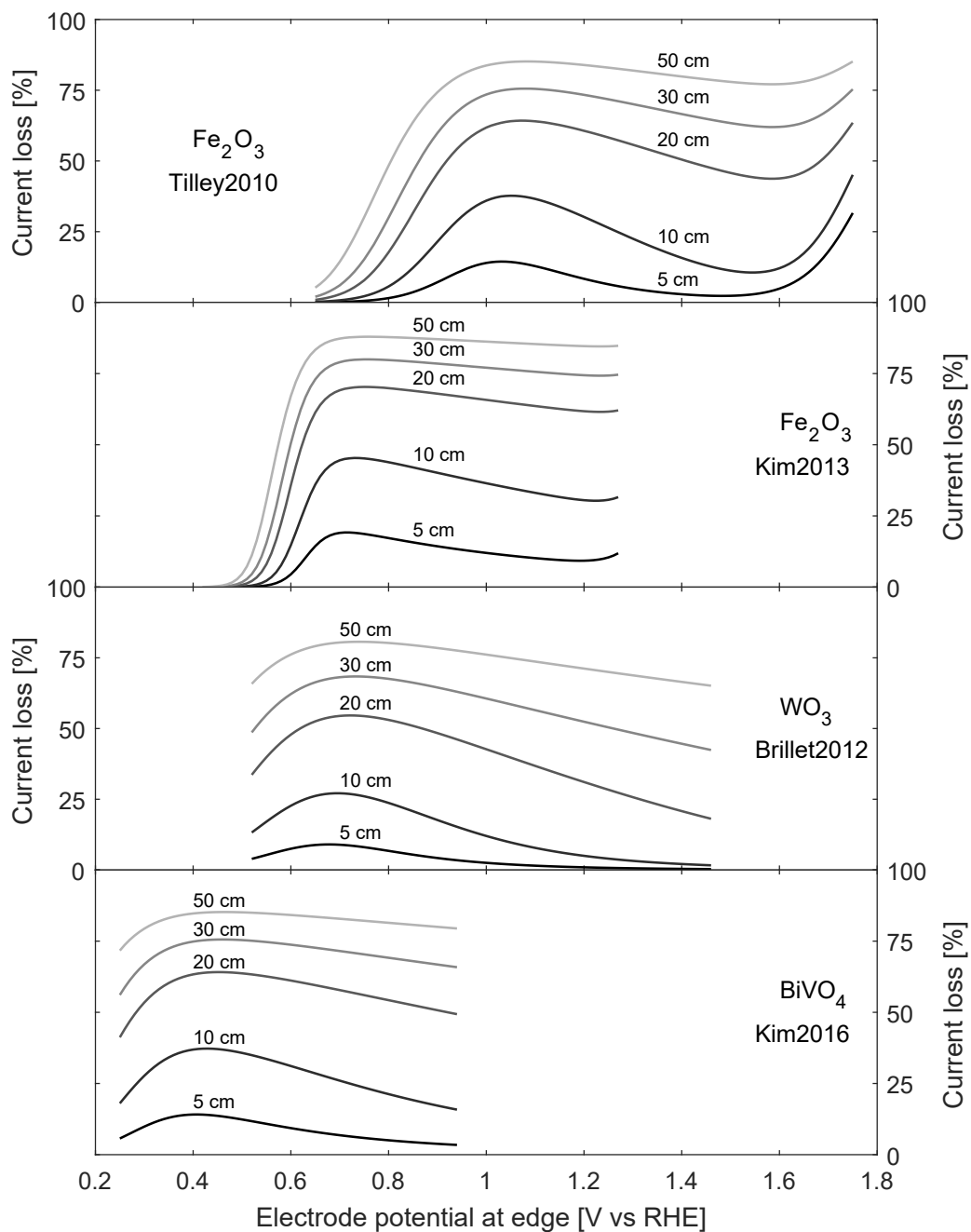


Figure 6.9: Current lost compared to an infinitely small photo-electrode at various electrode widths for Tilley2010 (Fe₂O₃), Kim2013 (Fe₂O₃), Brillet2012 (WO₃) and Kim2016 (BiVO₄) datasets

increase was not considered and the conductivity of the FTO was assumed to not be a function of light intensity (*i.e.* constant).

Figure 6.10 shows the logarithmic dependence of current lost due to substrate performance against solar concentration. This affirms that even for low solar concentration, the substrate performance may become a limiting issue.

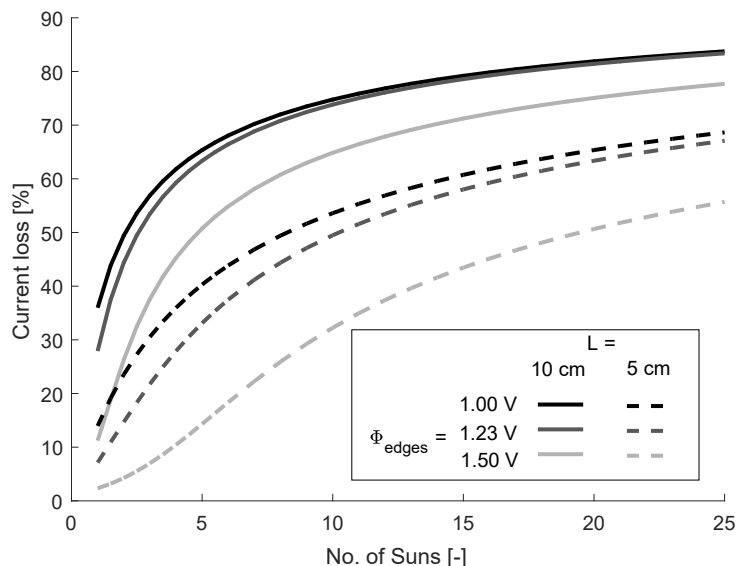


Figure 6.10: The current lost due to substrate resistivity *versus* the solar concentration using the Tilley2010 dataset (Fe_2O_3)

6.4.2 Trade-off between maximum power point and reducing current loss

A maximum power point potential can be defined for photo-anodes, in a manner analogous to the definition for PV [58], but *versus* the redox potential of water oxidation. It is clearly desirable to operate at the maximum power point potential shown in Figure 6.11.

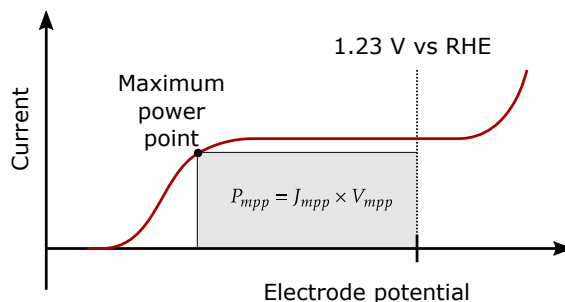


Figure 6.11: Diagram of maximum point for a photo-anode *vs.* the redox potential of water oxidation

However, as seen in Figure 6.12, the maximum power point potential corresponds to the greatest current lost due to substrate potential drop. Whereas, the current lost due to substrate resistivity is minimised by operation at higher potentials. As both are desirable criterion, there may be a trade-off between the two and operation at an electrode potential slightly greater than the maximum power point may be a suitable compromise.

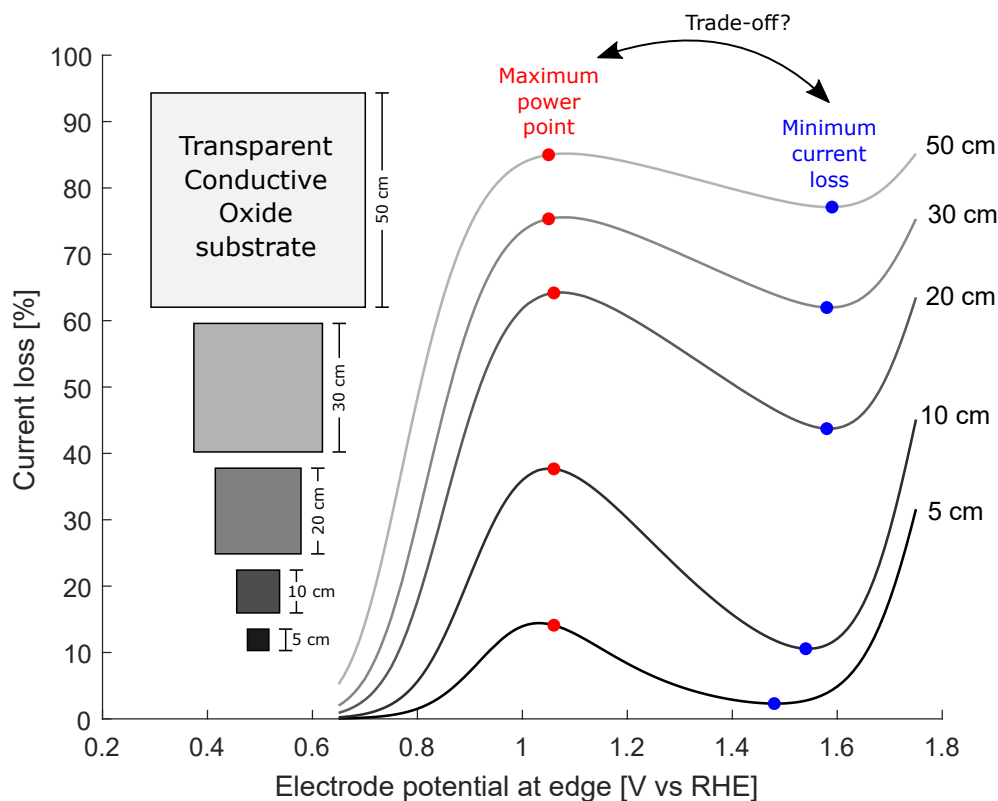


Figure 6.12: Current lost due to substrate resistivity as compared to an ideal substrate (infinitely conductive) as a function of electrode potential applied at edge of substrate. The maximum power point and the minimum current loss are denoted by red and blue dots respectively. Here, the maximum power point is defined as the electrode potential which maximises the power captured *vs.* the redox potential of water oxidation (see Fig. 6.11)

Ultimately, the system efficiency is a key driver in economic viability [31, 199] and a definition for the overall system efficiency or total input energy to hydrogen efficiency (η_{ETH}) is found in Eq. (6.11) (in accord with definitions previously reported [1, 58, 109]).

$$\eta_{ETH} = \frac{\varphi_{H_2} G_{f,H_2}^\circ}{P_{solar} + P_{bias} + P_{other}} \quad (6.11)$$

Therefore, the operation potential may be dictated by the overall system efficiency, where operation at the minima of current lost will require a higher bias which in turn

may reduce the overall system efficiency. For devices that are not externally biased (*i.e.* $P_{bias} = 0$), but ‘self-biased’ through coupling with another photo-electrode or solar cell, the operating electrode potential of the photo-electrode will be constrained by the current-voltage relationship of the other subcells. Hence, the design of the whole system may be influenced by the issue of substrate performance for the photo-electrode as subcells in series will be ‘current matched’. This extra photo-voltage required will, in turn, affect the optimal bandgaps and detailed balance limit efficiency (See Chapter 3). Therefore, this analysis demonstrates that for any scaled up design that relies on transparent conductive oxides such as FTO, either a complete assessment of system efficiency which includes the effects of substrate resistivity is required or the implementation of a mitigation strategy, which would allow this issue to be neglected.

6.5 Strategies for scaling up photo-electrodes

In this section, various strategies for scaling up photo-electrodes based on poorly conductive TCOs are proposed and critically evaluated.

6.5.1 Operate within constraints of TCOs

Losses could be slightly reduced, by electrical connection to all four edges of the square, but substrate performance would remain a challenge. Therefore, in order to operate within the constraints of TCOs, the photo-electrode size must be constrained to small area and/or the maximum allowable current density restricted. In this manner, one could ensure that the substrate performance is not limiting and the vast majority of present experimental reports into materials fall into this category with typically small electrode areas. Unfortunately, this has the obvious draw back that the task of scaling up many small area devices (cm^2) to span vast areas (km^2), in order to create a significant amount of fuel, will be a noteworthy challenge [106].

Furthermore, a 10% Solar-To-Hydrogen efficiency, which is a commonly quoted target for commercialisation [14, 31], corresponds to 81 A/m^2 for 1 Sun. It has been demonstrated in Figure 6.10 that such current densities will suffer catastrophic current losses due to substrate potential distribution. One solution to reduce the current density flowing through the photo-electrode could be to stack multiple photo-electrode optically in series, in a manner reported previously [81, 82] and discussed in Chapter 7. This would have the additional benefit of more efficient capture of light spectrum *via* multiple different bandgaps.

6.5.2 Improve substrate conductivity

Larger area substrates could be accommodated by using a more conductive substrate. ITO would be an obvious replacement for FTO due to its higher conductivity but ITO is unfortunately more expensive (due to the material scarcity of indium) and is less stable at the temperatures commonly encountered during metal oxide deposition and annealing. Metal substrates will have a significantly higher conductivity than TCOs, but may not form an ohmic contact (*i.e.* form a Schottky junction) especially with photo-anode materials. Furthermore, the transparency of TCOs is occasionally an integral feature of the PEC design when backside illumination or optically stacked photo-electrodes are used.

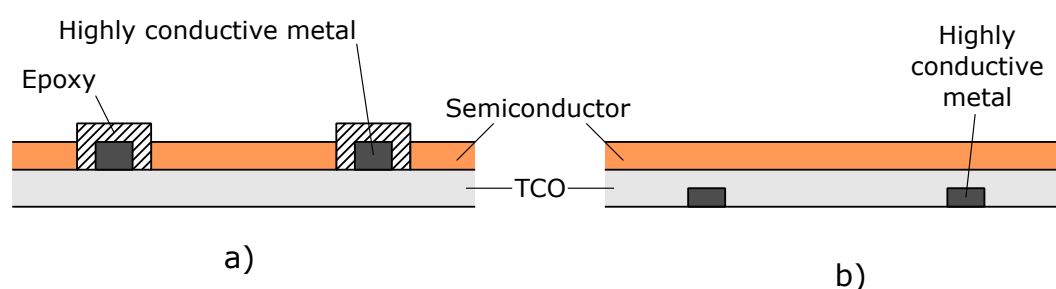


Figure 6.13: Diagram showing two hybrid substrate approaches in order to improve current collection: a) metal embedded into semiconductor and encapsulated b) metal embedded into TCO

If TCOs must still be used, then a hybrid substrate approach could be taken as shown in Figure 6.13. This would involve two materials: a film of TCO and ‘fingers’ of highly conductive material such as gold or silver. Current collection has been widely studied in the PV field where the hybrid approach suggested here is analogous to back contacts. This methodology has been employed for dye sensitised solar cells [235, 236] and thin film solar cell modules [217], but has received relatively little attention for PEC cells where it has been discussed theoretically by Farivar [133] and a similar methodology demonstrated for Ag fingers with WO_3 [237]. Care must be taken to ensure that the highly conductive material is either stable in the electrolyte at the electric potentials experienced or suitably encapsulated to ensure the metal does not contribute to the electrochemical current *via* oxidation. Gold is electrochemically stable at the pH and electrode potentials used, whereas silver is not. Therefore, in the work of Lee *et al.* [237], the loss of available surface area is compromised for the improved current collection as it is required that the Ag fingers are encapsulated with epoxy. Such a hybrid substrate approach could be highly scalable but may be complex to manufacture.

6.5.3 Apply a higher potential at the edges

As discussed previously and shown in Figure 6.12, there is a trade off between operating at the maximum power point potential and the potential which minimises the current lost due to substrate ohmic losses. Applying a higher bias potential at the edges of the photo-electrode is easily implemented, and will reduce the current lost. This approach is not applicable when a Tafel relationship is used for the electrode kinetics and therefore demonstrates the advantage of this more accurate model over previous attempts [131, 133].

6.6 Conclusions

- Previous modelling attempts fail to capture the realistic behaviour of semiconductor-electrolyte junctions and the model outlined here captures the behaviour of typical metal oxide photo-anodes more accurately.
- There will be a significant electric potential distribution due to substrate resistivity and therefore a substantial photo-inactive area for larger areas (square edge length $L > 5$ cm) photo-electrodes based on state of the art metal oxide on FTO substrates.
- Use of FTO as a substrate is even more unsuitable for large area devices operating under solar concentration.
- Due to the unique shape of the current-potential curve for the semiconductor-electrolyte junction, the current lost compared to an infinitely small electrode rises with increasing electrode potential to a maximum (at the mpp potential) before falling to a minimum as the photo-current saturates. If the dark current is observable, the losses then continue to rise with increasing electrode potential applied at the edges. This means that there is a trade-off between operating at the maximum power point and reducing the ohmic losses in the substrate.
- There are many strategies for overcoming or circumventing this scaling issue. Notably, a hybrid substrate approach would render TCO extremely scalable, where highly conductive metal fingers could extract the charge from the FTO.
- No general heuristic for limiting electrode size is given as it is demonstrated that the current losses are dependant on the complex combination of substrate conductivity, semiconductor-electrolyte junction performance, the solar concentration, and location of electrical connection amongst other things. Furthermore, what constitutes an 'acceptable' current loss is a matter of economic study. Therefore, the uncomplicated model is provided as a way to easily and accurately compute losses specific to each scenario.

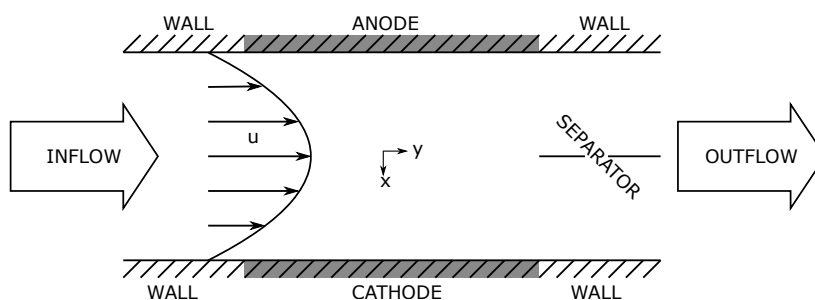
Chapter 7

Membrane-less PEC: Theory and simulation

The goal of good photo-electrochemical reactor design is to reduce the energetic losses which will minimise the required photo-voltage from the semiconductor-electrolyte junction. This chapter outlines a membrane-less design in which dissolved hydrogen and oxygen produced at two opposing flat plate (photo-)electrodes is separated *via* forced convection in a laminar electrolyte flow. A numerical simulation of the cell along with dimensionless analysis was used to evaluate the general behaviour. A more complete multiphysics model (optics + current density distribution + mass transport) was then used to validate this and investigate efficiency gains from multiple membrane-less reactors stacked.

This chapter is partially based on the author's publications:

[1] I. Holmes-Gentle *et al.*, "Membrane-Less Photoelectrochemical Cells: Product Separation by Hydrodynamic Control", *Sustainable Energy Fuels* **2017**, *1*, 1184–1198 - Reproduced with permission from the Royal Society of Chemistry.



7.1 Introduction

As discussed in Chapter 4, there are a number of designs considered for scale up, each with their own advantages and disadvantages. The reactor must 1) separate products (H_2 and O_2) 2) minimise ion path length between electrodes to reduce ohmic losses 3) maximise the efficiency of light capture and utilisation (minimise parasitic optical losses/reflection losses) [131].

Product separation is typically achieved by separating the two half reactions with an ion permeable membrane. Whilst an established technology in the field of PEM electrolysis and fuel cells (*e.g.* Nafion®), there will need to be significant advances in the conductivity, stability and cost of anion exchange membranes [238] in order for alkaline membrane PEC systems to be feasible. Membrane product separation incurs an energetic loss in the form of a ohmic drop [167] and there will be a compromise between the gas cross-over and the ionic conduction of the membrane [136, 239]. Additionally, such membranes can be comparatively expensive [112, 240]. Another common constraint with membranes is that as they are typically not optically transparent, they must be placed so as they do not optically block the electrode, whilst the physical arrangement must simultaneously ensure that the ionic path length and current density distribution is minimised. As mentioned in Chapter 4, a number of methods have been proposed or demonstrated in order to overcome these challenges (*e.g.* louvered-design [137], perforated photo electrode [107, 109]).

In this chapter a novel and relatively unexplored PEC device, namely one that removes the membrane from the system and so eliminates the aforementioned challenges, is investigated. However, any membrane-less PEC reactor substitutes the compromises associated with membrane placement and cost with inherent challenges in efficient product separation and safe operation of the cell. One notable mention of a membrane-less PEC device that utilised bubble buoyancy as the method of product removal suffered untenable levels of product cross-over [136].

The use of forced convection to facilitate product separation has been investigated for a range of membrane-less electrochemical devices such as electrolyzers [125, 241] to fuel cells/redox batteries [242–247]. To the best of our knowledge there has not been the theoretical investigation or application of this technology for PEC devices. Indeed, mass-transfer control through manipulation of the hydrodynamics may actually be less challenging due to the typically low current densities at which PEC devices operate at in comparison to electrolyzers [167], as the PEC device current density is inherently limited by the solar resource and the amount of solar concentration.

The following chapter is laid out as follows:

- A membrane-less PEC reactor design is proposed
- The fundamental mass transfer behaviour is established for an idealised scenario: constant reaction flux electrode
- A multi-physics model is developed to simulate the realistic performance for a typical PEC materials (Fe_2O_3).

7.2 Proposed design

7.2.1 Membrane-less product separation *via* hydrodynamic control

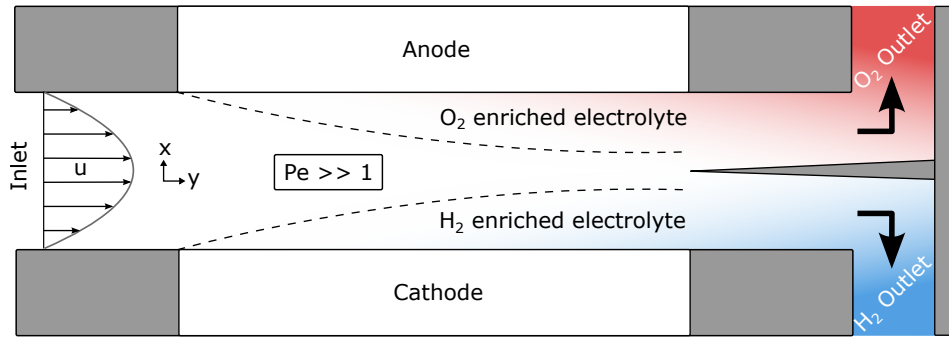


Figure 7.1: Example diagram of membrane-less PEC cell

The membrane-less PEC cell shown in Figure 7.1 is designed to stop the evolved hydrogen and oxygen from mixing through the careful engineering of the fluid mechanics of the system. Forced convection ensures that dissolved gases are transported out the cell *via* their respect outlet faster than they can meet through diffusion. The flow separator (placed at the centreline) splits the fluid flow into two streams, one containing H_2 and the other containing O_2 . Product cross-over must be minimised as it will not only lead to lower product collection efficiencies, but constitute a safety hazard as H_2 is highly flammable in O_2 (LFL = 4 vol%, UFL = 94 vol%, in O_2 at 1 atm).

The performance of this membrane-less design will be dependent on competition between convective forces in the direction of fluid flow and diffusive forces. Therefore, among other dimensionless parameters, the Péclet number Pe will be important where Pe is defined in Eq. (7.1) as the ratio of advective transport rate over the diffusive rate. For a system in which the convective forces dominate (when $Pe \gg 1$), the transport of dissolved gases can be controlled by the fluid mechanics of the system.

$$Pe = \frac{L_x \langle u_y \rangle}{D} \quad (7.1)$$

The vortices characteristic of turbulent flow, would increase mixing perpendicular to the fluid flow which contradicts the goal of product separation. Therefore, a laminar flow is necessary. The key dimensionless number which governs the fluid flow regime is the Reynolds number Re defined in Eq. (7.2) and the flow between infinite parallel plate will be laminar for $Re < 2000$.

$$Re = \frac{\rho \langle u_y \rangle L_x}{\mu} \quad (7.2)$$

This membrane-less design relaxes a crucial material constraint when compared to other more conventional membrane designs: A reduced photo-voltage required to split water as both the ion path length through the electrolyte is small and there are no ohmic losses through the membrane. As shown in Chapter 3, the reduction of photo-voltage is particularly crucial for system with a semiconductor-electrolyte junction, where an increased photo-voltage due to higher bandgap often comes at the expense of a reduction in the amount of solar spectrum captured. Nonetheless, there are unique challenges associated with this membrane-less design. Firstly, ensuring product separation becomes a far more complicated task than in the case of a membrane PEC reactor. Secondly, for the front side illumination of a photo-anode, the cathode must be transparent and *visa versa* for a photo-cathode configuration. Furthermore, this design removes capital cost (the cost of the membrane) and replaces it with operating cost (the fluid must be pumped continuously), and a full economic study would be required to assess the effect on the final production price of hydrogen.

7.2.2 Stackable design

Figure 7.2 shows four cells (Fig. 7.1) stacked together, normal to the incoming light. In this configuration, this means the first cell need not absorb all the light, as unabsorbed light can be absorbed by the next cell and this could increase the overall efficiency. Stacking multiple electrode then relaxes another common material constraint for metal oxide semiconductors, that the photo-absorber should both absorb a significant amount of light whilst maintaining a high carrier collection efficiency. Commonly, nanostructuring is used to improve the performance of metal oxide materials, by reducing the average path length of charges from excitation to the electrochemical surface [248].

Through stacking, the requirement for a simultaneously high absorption coefficient and a large carrier path length of the exited charges is relaxed, and the overall Incident Photo to Current Efficiency ($IPCE$) and the overall Absorbed Photo to Current Efficiency ($APCE$) is decoupled. The stacked design could realise high STH efficiencies

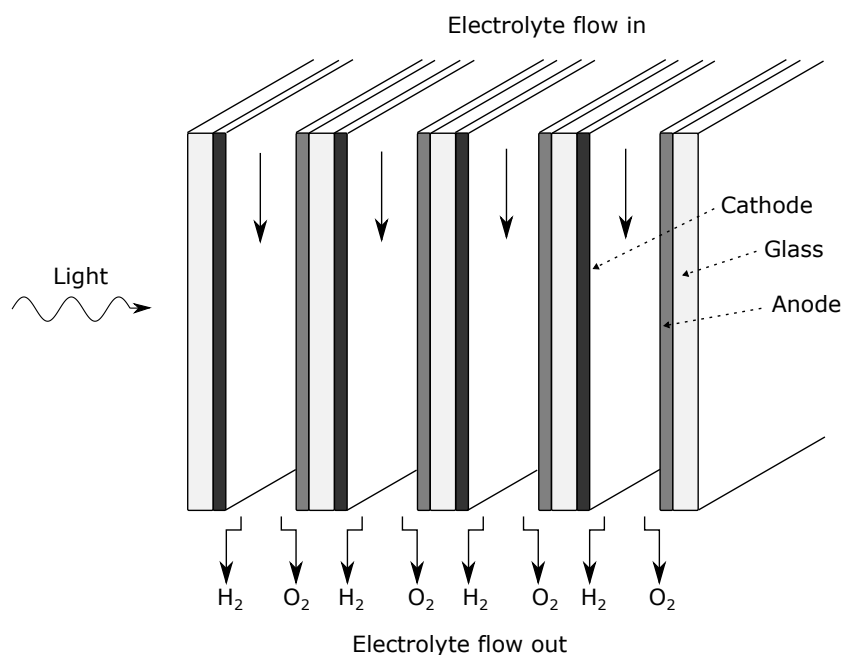


Figure 7.2: Stacked membrane-less PEC design

for materials which have a high *APCE* (absorbed light is efficiently used) but low *IPCE* (doesn't absorb much light) for single pass of light, without the need for nanostructuring. For example, a 9 nm thick ultra-thin hematite film which has achieved a high *APCE*, *ca.* 44%, but suffers from a low absorptance, *ca.* 20%, at 400 nm wavelength light [249], may benefit from this stacked design.

In fact, a similar stacked design has already been proposed for this very reason by Itoh and Bockris [250, 251]. They demonstrated that stacking photo-electrode improved the total photo-current but their design will suffer from current density distribution issues at scale.

This stacked design will likely benefit from process intensification through optical concentration and pressurisation. The stacked cells are comparable to other commercial equipment such as flat plate heat exchangers and fuel cells/electrolysers where pressurisation is easily achieved. For PEC devices, pressurisation could be desirable as it will suppress bubble formation, and could reduce the downstream compression costs. Large area PEC systems may be harder to compress than for a PEC reactor with a small aperture area, and so the cost of pressurisation may be offset by concentrating the light, though this would be a point for further economic study in the future.

7.3 Theory

As mentioned previously, there will be two models constructed. The first a generic mass transport model assuming a constant electrode flux. Secondly, a multi-physics

model which relaxes the assumption of constant electrode flux and simulates both the ionic charge transport and optics of the system for an example metal oxide material: Fe_2O_3 .

7.3.1 Fluid mechanics

An analytical solution for the fluid mechanic between two infinite parallel plates can be found if the flow is laminar. This is derived from the incompressible Navier-Stokes equation given in Eq. (7.3) which is fundamentally a momentum balance, and the incompressible continuity equation ($\nabla \cdot \mathbf{u} = 0$) which is a mass balance. Here, the fluid velocity vector is denoted by $\mathbf{u}$. Water can be assumed to be completely incompressible at the experimental temperature and pressures.

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla P + \mu \nabla^2 \mathbf{u} + \rho \mathbf{g} \quad (7.3)$$

For low Reynold numbers ($\text{Re} < \sim 2000$), the flow will be laminar which as, described later, is key to the efficacy of a membrane-less water splitting *via* forced convection approach. Therefore, by specifying laminar flow and neglecting the gravitational term in the Navier-Stokes equation, an analytical solution for the fluid velocity of laminar flow between infinite parallel plates that are separated by distance L_x can be found: Eq. (7.4).

$$u_x = 0, \quad u_y = \frac{1}{2\mu} \Delta P_{drop} (L_x x - x^2) \quad (7.4)$$

From Eq. (7.4), both the average velocity and the total flow rate can be calculated by Eq. (7.5) and Eq. (7.6) respectively. Here, the depth of the channel is denoted as L_z .

$$\langle u_y \rangle = \frac{L_x^2}{12\mu} \Delta P_{drop} = \frac{2}{3} u_{y,max} \quad (7.5)$$

$$\dot{Q} = L_z L_x \langle u_y \rangle \quad (7.6)$$

7.3.2 Mass transport

The molar flux N_i of the dissolved gas i , can be given by Eq. (7.7) as the summation of flux due to diffusion and the flux due to convection assuming the species are dilute. Here, D_i is the diffusivity, c_i is the concentration of dissolved species i . The fluid velocity vector $\mathbf{u}$ is determined through the solution of the aforementioned fluid mechanics.

From this equation and the molar continuity equation (Eq. (7.8)), where R_i is the reaction rate, the mass transfer of the dissolved species i can be determined.

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i \quad (7.7)$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{N}_i) = R_i \quad (7.8)$$

In the bulk fluid, negligible reaction of H_2 and O_2 is assumed as the reaction rate is far slower than the residence time of the reactor [252] and that the concentration of H_2 and O_2 should never be simultaneously high, by virtue of the design. Steady state is assumed, which means that $\partial c_i / \partial t = 0$. The final simplifying assumption is that the diffusivity is independent of position in the reactor and that the electrolyte is incompressible ($\nabla \cdot \mathbf{u} = 0$) and hence Eq. (7.8) can be expressed as Eq. (7.9). Here, $\mathbf{u}$ is the velocity vector and u_y is the only non-zero component determined from the fluid mechanics.

$$0 = D_i \nabla^2 c_i - \mathbf{u} \nabla \cdot c_i = D_i \frac{\partial^2 c_i}{\partial x^2} + D_i \frac{\partial^2 c_i}{\partial y^2} - u_y \frac{\partial c_i}{\partial y} \quad (7.9)$$

Hydrogen and oxygen are produced at the electrodes, on the boundary of the domain. This is therefore specified as a boundary condition where the molar flux at the electrode can be related to the current density by Faraday's law given in Eq. (7.10).

$$R_{anode/cathode} = \frac{\eta_f \dot{j}_{anode/cathode}}{n_e F} \quad (7.10)$$

7.3.3 Charge transport

Current density distribution model

Current density distribution models fall into three categories.

1. Primary: Neglecting kinetics and mass transfer
2. Secondary: Neglecting mass transfer
3. Tertiary: Including both electrode kinetics and mass transfer

In this chapter, a secondary current density distribution model is used as the kinetics are not fast enough to be neglected but mass transfer is not an issue due to both the high concentration of reactants (1 M NaOH). Notably, this can be validated by checking that the currents simulated are below the theoretical limiting current density between two flat plates which is given by Eq. (7.11) [138]. Here, the position on the electrode

from the start of the electrode relative to the fluid flow is denoted by x , and s_i is the stoichiometric coefficient of species i in the electrode reaction.

$$j_{lim} = 0.9783 \frac{n_e F D_i c_\infty}{s_i} \left(\frac{\langle u_y \rangle}{L_x D_i x} \right)^{1/3} \quad (7.11)$$

Assuming electro-neutrality of the electrolyte, the conservation of current density leads to the so called Laplace's equation (Eq. (7.12)). Similar to the mass transfer model, the electrochemical reaction appears as a boundary condition, namely $\nabla \Phi = -j_{electrode}/\kappa$ where $j_{electrode}$ is the current at the electrode given by electrode kinetics. For an insulating boundary $\nabla \Phi = 0$.

$$\nabla \mathbf{j} = 0, \quad \mathbf{j} = -\kappa \nabla \Phi, \quad \nabla^2 \Phi = 0 \quad (7.12)$$

Electrode kinetics

As a secondary current distribution model was employed, information on the electrode kinetics is required. That is, the relationship between the inner potential of the electrode and the current density at the electrode surface.

A simplistic Butler-Volmer type relationship can be used for metal-electrolyte interfaces as given in Eq. (7.13) where $f = F/RT$. The electrode potential E is relative to some reference electrode and can be related to the absolute electric potential scale by $E = \Phi_{electrode} - \Phi + \text{constant}$ where $\Phi_{electrode}$ and Φ is the electrode and electrolyte absolute potentials respectively. The constant originates from the type of reference electrode system used and, as it would cancel out in Eq. (7.13), it is not specified.

$$j_{electrode}(E) = j_o \left(e^{\alpha_a f (E - E_{eq})} - e^{-\alpha_c f (E - E_{eq})} \right) \quad (7.13)$$

On the contrary, the kinetic relationship at semiconductor-electrolyte interfaces is far more complex and describing the current-voltage relationship with a single analytical equation, derived from the fundamental physics, is restricted to only the most ideal cases. For example, Gartner's model [220, 225] neglects both the space charge layer and surface recombination, which is not valid for low performing semiconductors such as hematite. Various attempt to include this recombination have been made [221, 253], but suffer from a lack of accurate values on the fundamental properties [14]. Numerical solution of the semiconductor equations may provide more realistic models [228–230, 252] but are complex and computationally intensive.

In light of this, a simplistic approach was taken using experimental data which then provides the model with realistic photo-electrode kinetics. The total photocurrent for

a given spectrum of light was calculated from the integration of empirical Incident-Photon-to-Current-Efficiency (IPCE) data for both the forward and backward illuminated light (Eq. (7.14)). This assumes that the photocurrent is linear with the total light irradiance for a given spectrum.

$$j_{photo}(E) = \int_0^\infty q_e (\eta_{IPCE}^f q_p^f + \eta_{IPCE}^b q_p^b) d\lambda \quad (7.14)$$

The IPCE, sometimes referred to as the external quantum efficiency, is a function of wavelength λ , illumination direction and electrode potential E and is calculated *via* Eq. (7.15). The spectral photon flux q_p can be calculated from the spectral irradiance E_λ using Eq. (7.16) where h , q_e and c is the Planck constant, fundamental positive charge and the speed of light respectively.

$$\eta_{IPCE}(\lambda, E) = \frac{1}{q_e q_p(\lambda)} \left(\frac{\partial j_{photo}(\lambda, E)}{\partial \lambda} \right) \quad (7.15)$$

$$q_p(\lambda) = \frac{\lambda}{hc} E_\lambda(\lambda) \quad (7.16)$$

7.3.4 Photon transport

The modelling of photon transport and absorption through the system is achieved using a mixed incoherent and coherent transfer matrix method which similar to previous descriptions [254–256]. The most simplistic optical model available would be the Beer-Lambert law but the transfer matrix method has the advantage of more realistically simulating the behaviour of light on interaction with multiple layers and describes the interference and multiple reflections within the material [257]. For more complex geometry, solution of Maxwell's equations in the full three dimension would be required, but for the requirements of this model, this would be superfluous.

The transfer matrix method accounts for multiple reflections and absorption in the different layers, by using an ideal 1D solution to Maxwell's equations. This is particularly useful as the parasitic absorption losses by the glass, electrolyte and other PEC components can be quantified. Henceforth, in order to reduce complexity only equations relating to s-polarisation are given. In the case of normal light incident upon the layers, this reduction in complexity is arbitrary as the polarisation of the light does not affect the transmittance, reflectance and absorptance. However, if non-normal incident light is considered, the light must be divided into two polarisation fractions and each solved independently.

For the formulation of the incoherent transfer matrix, the electric field intensity is used. This is calculated from the square of the amplitude of the electric field $U = |E|^2$ which

removes all phase information (*i.e.* incoherent model). The forward and backward propagating waves will each have an electric field intensity, denoted by U^+ and U^- respectively. Finally, Figure 7.3 introduces the positional notation used herein where each interface has two directions (*i.e.* forward, backward) and 2 positions (*i.e.* left and right).

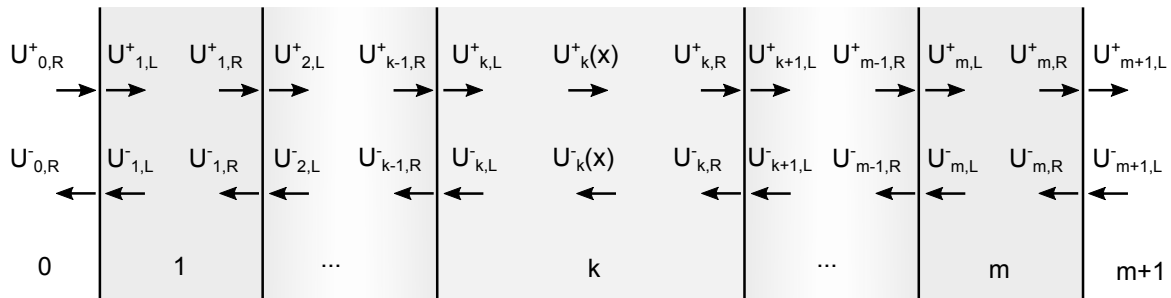


Figure 7.3: A cross-sectional diagram of multiple optical layers to display the layer and electric field intensity numbering

The forward and backward light components of the electric field intensity at either end of the stack of layers can be determined by matrix multiplication with a 2×2 matrix called the system transfer matrix $\bar{S}$ and this is given in Eq. (7.17). Furthermore, as shown in Eq. (7.18), the system transfer matrix can be broken down into its constituent individual parts relating to each interface and each layer in the stack. Each layer and interface can be represented by a 2×2 transfer matrix where the subscript gives the position. For example, $\bar{L}_1$ is the layer transfer matrix of the 1st layer and $\bar{I}_{1,2}$ is the interface transfer matrix of the interface between the 1st and the 2nd layer. As matrix multiplication is not commutative, the order matters and so must match the order of the layers.

$$\begin{bmatrix} U^+_{0,R} \\ U^-_{0,R} \end{bmatrix} = \bar{S} \begin{bmatrix} U^+_{m+1,L} \\ U^-_{m+1,L} \end{bmatrix} \quad (7.17)$$

$$\bar{S} = \bar{I}_{0,1} \bar{L}_1 \bar{I}_{1,2} \cdots \bar{L}_m \bar{I}_{m,m+1} \quad (7.18)$$

The layer transfer matrix $\bar{L}_k$ for the k^{th} layer is given by Eq. (7.19). The term $\beta_k = 2\pi d_k \tilde{n}_k / \lambda$ where d_k and $\tilde{n}_k$ are the thickness and the complex refractive index respectively, of the k^{th} layer of stack. Note the exponential relationship is similar to the Beer-Lambert's law.

$$\bar{L}_k = \begin{bmatrix} |\exp(-\beta_k \sqrt{-1})|^2 & 0 \\ 0 & |\exp(\beta_k \sqrt{-1})|^2 \end{bmatrix} \quad (7.19)$$

Equation (7.20) is used to calculate the interface transfer matrix $\bar{\mathbf{I}}_{k,k+1}$ of the interface between the k^{th} and the $(k+1)^{\text{th}}$ layer. The definitions of the complex transmission and reflection coefficients (t, r resp.) from forward and backward illumination (*e.g.* t^+, t^- resp.) are given in Eq. (7.21).

$$\bar{\mathbf{I}}_{k,k+1} = \frac{1}{|t^+|^2} \begin{bmatrix} 1 & -|r^-|^2 \\ |r^+|^2 & |t^+ t^-|^2 - |r^+ r^-|^2 \end{bmatrix} \quad (7.20)$$

$$r^+ = \frac{E_{k,R}^-}{E_{k,R}^+}, \quad r^- = \frac{E_{k+1,L}^+}{E_{k+1,L}^-}, \quad t^+ = \frac{E_{k+1,L}^+}{E_{k,R}^+}, \quad t^- = \frac{E_{k,R}^-}{E_{k+1,L}^-} \quad (7.21)$$

The complex transmission and reflection coefficients can be calculated with the Fresnel's equations for s-polarisation given in Eq. (7.22) and Eq. (7.23). The subscript notation a, b denotes that the light impinges on the interface from layer a and the layer after is b . Therefore, both directions of light (*i.e.* forward + and backward -) can be calculated using these two equation.

$$r_{a,b}^s = \frac{\tilde{n}_a - \tilde{n}_b}{\tilde{n}_a + \tilde{n}_b} \quad (7.22)$$

$$t_{a,b}^s = \frac{2\tilde{n}_a}{\tilde{n}_a + \tilde{n}_b} \quad (7.23)$$

Layers such as the electrolyte and glass were modelled as incoherent layers using the theory detailed above. In order to include thin films which may behave coherently (*e.g.* the photo-anode) into the incoherent model, these thin layers were reduced to a pseudo-interface for which an equivalent incoherent interface matrix was determined in a similar manner to reducing a 'packet' of coherent layers to an equivalent interface [254]. This approach was taken as the properties of the pseudo-interface could be measured and calculated from transmittance T and reflectance R data which ensure accuracy at the expense of obtaining a fundamental model from first principles. Equation (7.24) gives the equivalent interface where the definition of the intensity transmission and reflection coefficients (not complex) are given in Eq. (7.25) and using Eq. (7.26) can be calculated from the experimentally measured transmittance and reflectance.

$$\bar{\mathbf{I}}_{k,k+1}^{equiv} = \frac{1}{\bar{t}^+} \begin{bmatrix} 1 & -\bar{r}^- \\ \bar{r}^+ & \bar{t}^+ \bar{t}^- - \bar{r}^+ \bar{r}^- \end{bmatrix} \quad (7.24)$$

$$\bar{r}^+ = \frac{U_{k,R}^-}{U_{k,R}^+}, \quad \bar{r}^- = \frac{U_{k+1,L}^+}{U_{k+1,L}^-}, \quad \bar{t}^+ = \frac{U_{k+1,L}^+}{U_{k,R}^+}, \quad \bar{t}^- = \frac{U_{k,R}^-}{U_{k+1,L}^-} \quad (7.25)$$

$$R^+ = \bar{r}^+ \quad T^+ = \bar{t}^+ \frac{\text{Real}\{\tilde{n}_{k+1}\}}{\tilde{n}_k} \quad R^- = \bar{r}^- \quad T^- = \bar{t}^- \frac{\text{Real}\{\tilde{n}_k\}}{\tilde{n}_{k+1}} \quad (7.26)$$

For incoherent layers, as there is no interference, the optical power density, *i.e.* the Poynting vector, of a plane wave is given by Eq. (7.27) for both forward and backward moving light [258].

$$P_k^+ = \frac{1}{2}c\epsilon_0\text{Real}\{\tilde{n}_k\}U_k^+ \quad P_k^- = \frac{1}{2}c\epsilon_0\text{Real}\{\tilde{n}_k\}U_k^- \quad (7.27)$$

Finally, the net power density of light travelling forward can be determined Eq. (7.28) and the absorptance of a specific layer k can be calculated from (7.29) where x is the distance from the start of the layer and d_k is the thickness of layer k .

$$P_k = P_k^+ - P_k^- \quad (7.28)$$

$$A_k = \frac{P_k(x=0) - P_k(x=d_k)}{P_{0,R}^+ + P_{m+1,L}^-} \quad (7.29)$$

7.4 Description of models

Two models of various complexity were constructed:

1. Constant electrode flux mass transfer model - to investigate the fundamental competing processes (convection and diffusion) controlling the mass transport and quantify the operational design space where product separation is achieved
2. Multi-physics model - used to both justify assumptions made in the first model and to investigate the realistic performance of a membrane-less cell with a Fe_2O_3 photo-anode

For both models, a custom MATLAB script was used for the numerical solution of the partial differential equations. In order to verify the code, the mass-transfer only model was compared against a commercial finite element solver (COMSOL).

7.4.1 Constant electrode flux mass transfer model

A generic model was set up that only included the mass transfer and fluid mechanics of the membrane-less cell and specified a constant flux at the surface of the electrode, in order to study the general operational behaviour of the system using dimensionless analysis. Furthermore, this type of study requires no specific parameters which means any conclusions drawn are not constrained to one particular case.

Figure 7.4 shows the domain equation and boundary conditions superimposed on the geometry considered. Here, the fluid velocity in the y direction u_y is calculated using the analytical solution for laminar flow between two infinite flat plates (Eq. (7.4)). The

molar rate of reaction at the surface can be related to the electrode current density by assuming a faradaic efficiency of unity and then using Eq. (7.10).

For the constant electrode flux mass transfer model, the boundary conditions are as follows. At the inlet, the concentration of species i is specified ($c_i = c_{i,0}$) and at the outlet, the derivative is specified ($\frac{\partial c_i}{\partial y} = 0$). The flux (normal to the surface) of species i at the non-reactive walls is zero ($N_{i,x} = 0$). For the electrodes, the flux normal at an electrodes that produces species i is equal to the surface reaction rate ($N_{i,x} = R_{i,electrode}$), whereas if the electrode consumes the species (*i.e.* oxidation of hydrogen, reduction of oxygen), it is assumed the reaction is fast and hence concentration at the electrode surface is equal to zero ($c_i = 0$). The surface reaction rate can be related to the current density *via* Faraday's law.

A more complete mathematical description of model and the details of the discretisation can be found in Appendix 11.4.

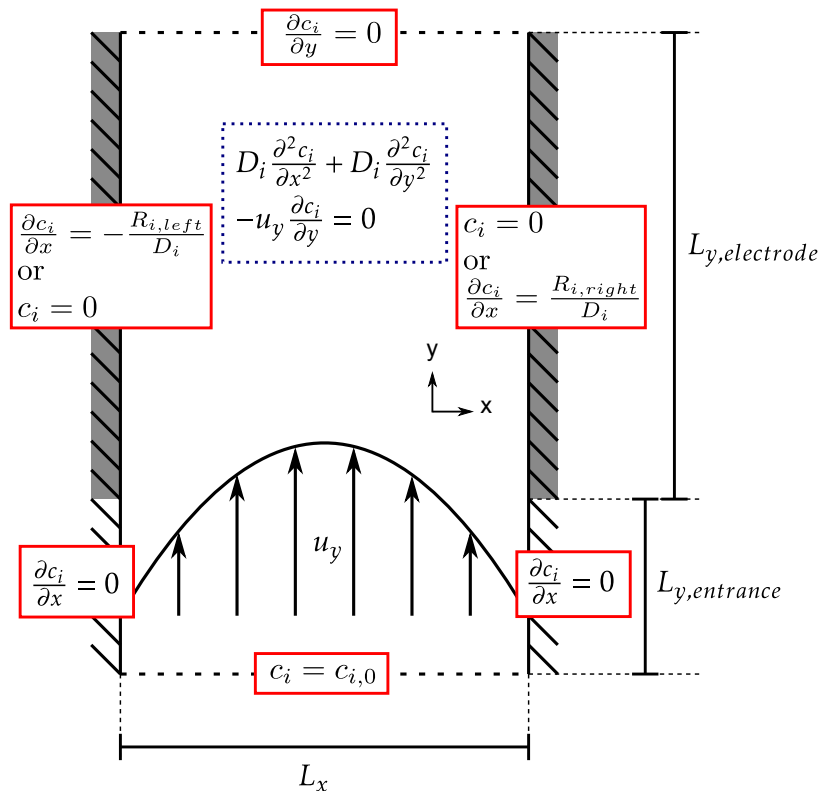


Figure 7.4: Equations, geometry and boundary conditions of the mass transfer model

7.4.2 Multi-physics model

Whilst the first model (constant electrode flux mass transfer model) will be used to investigate the generic behaviour, the multiphysics model is used to simulate a specific example. The motivation then for the more complete multiphysics model was to

validate conclusions drawn from the constant electrode flux model and investigate feasible reactor dimensions. It also permits the quantification of optical parasitic losses and to model the stacked design which incorporates multiple membrane-less cells optically in series.

Figure 7.5 displays the multiphysics model hierarchy, showing the transfer of results. As each of the models are uncoupled, they are executed sequentially where the optical model (transfer matrix method) provides the irradiance that falls upon the photo-electrode to the current density model which in turn provides the current density distribution on the electrode to the mass transfer model.

The mass transfer model matches the one used for the constant electrode flux mass transfer model (Fig. 7.4). This is uncoupled to the current density distribution model as this neglects the mass transfer of the ions in solution. The model equations, boundary conditions and geometry are displayed in Figure 7.6. The optical model is entirely algebraic and computed before the solution of the charge and mass transfer models. More complete details on the solution process for the multiphysics model, including the discretisation scheme used, can be found in Appendix 11.4.

Model parameters/experimental details

In order to model the membrane-less cell for a specific example, electrode and electrolyte properties were selected. The photo-electrochemical cell selected, shown in Figure 7.7, comprises of a planar thin film hematite ($\alpha\text{-Fe}_2\text{O}_3$) photo-anode, 1 M NaOH electrolyte and cathode composed of a thin film of Pt on FTO. Hematite was chosen due to its absorption of visible light, stability in alkaline electrolytes and linear dependence of the photocurrent with irradiance [231] which facilitates the use of the theory outlined previously to be used (*cf.* Eq. (7.14)). Whilst $\alpha\text{-Fe}_2\text{O}_3$ is a low performing material and requires an electrical bias to split water, it can be used for the preliminary calculations of technical feasibility of the membrane-less cell and future work could investigate other semiconductor-electrolyte junctions as the model is not material specific.

Wherever possible, data was taken from literature: *e.g.* diffusivity of products, conductivity of electrolyte *etc.* However, for Fe_2O_3 and Pt thin films, data was not widely available on both the optical and (photo-)electrochemical properties for the same sample. Therefore, these properties were experimentally determined.

The experimental cell construction is outlined as follows. The electrolyte used is 1 M NaOH and due to its high concentration of OH^- it possesses high conductivity and high limiting current density (*cf.* Eq. (7.11)). It also ensures pH uniformity within the cell, which is not necessarily the case for near neutral electrolytes [136]. The photo-anode material, Fe_2O_3 , was deposited using spray pyrolysis of an EtOH solution containing

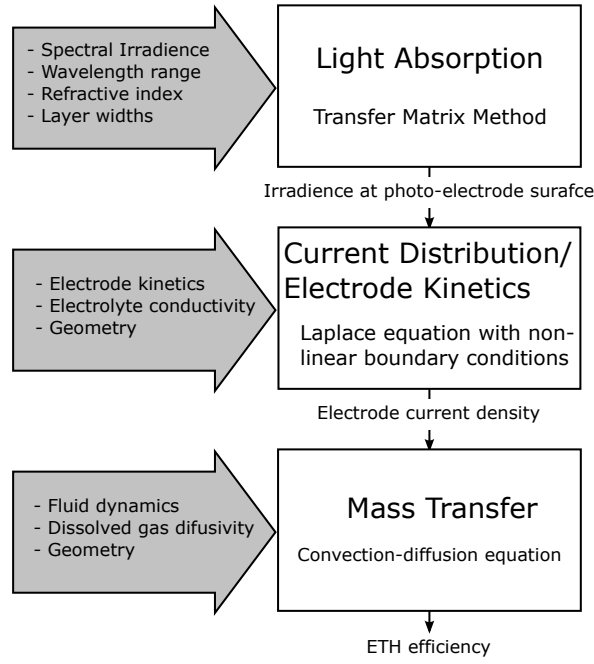


Figure 7.5: Components of multi-physics model showing the model hierarchy and the inputs/outputs of each physics

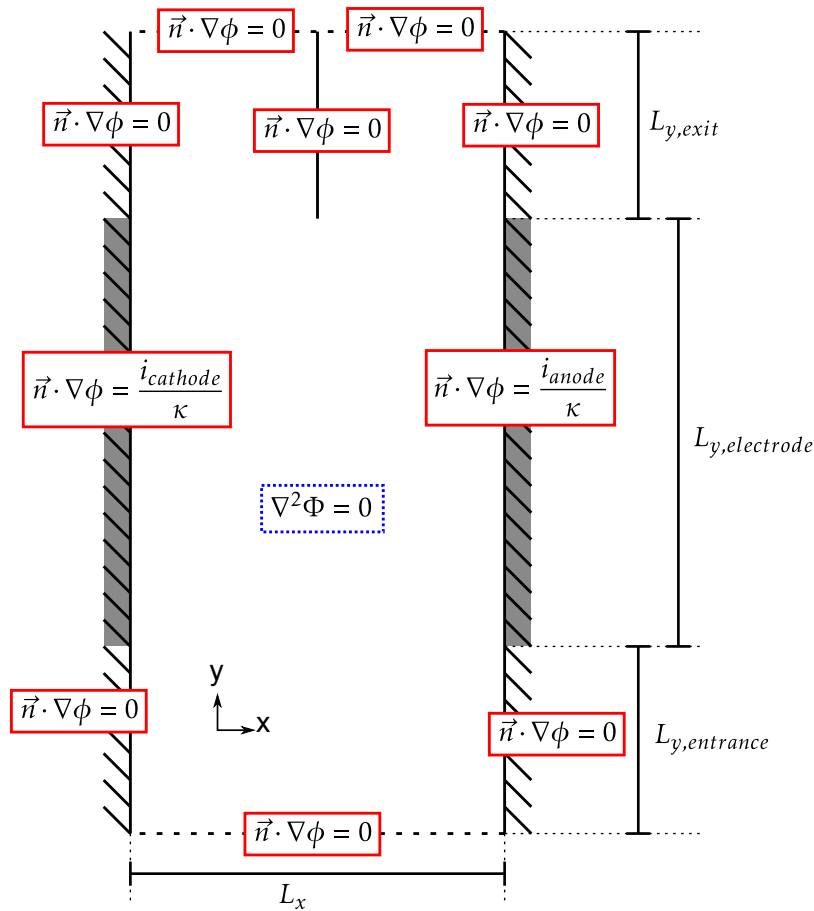


Figure 7.6: Equations, geometry and boundary conditions of the secondary current density distribution model

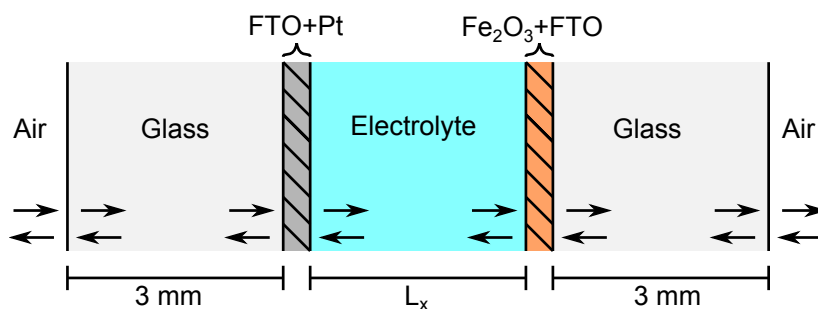


Figure 7.7: Optical geometry of one photo-electrochemical cell

$50 \text{ mol dm}^{-3} \text{ FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $0.3 \text{ mol dm}^{-3} \text{ SnCl}_2 \cdot 2\text{H}_2\text{O}$. This was deposited directly onto the fluorine doped tin oxide (FTO) glass slide (Pilkington TEC $8 \Omega\text{sq}^{-1}$) heated to approximately 470°C on a hot plate. The sample was then annealed in a furnace (open to atmospheric air) at 500°C for 1 hour. As the photo-anode may be illuminated from the front, this design requires the cathode material to be transparent. In order to achieve this, a thin layer of platinum nano-particles was deposited on a FTO glass slide *via* dip coating in a $1 \text{ mol dm}^{-3} \text{ H}_2\text{PtCl}_6$ in 2-propanol solution. A procedure similar to Papageorgiou *et al.*[259] was repeated twice to obtain an approximate loading of $0.1\text{--}1 \mu\text{g cm}^{-2}$: 1) the sample was dipped in solution and withdrawn at room temperature 2) the solvent was allowed to evaporate 3) the sample was annealed in a furnace at 385°C for 15 mins.

The photo-electrochemical performance of the Fe_2O_3 photo-anode was experimentally determined using photo-current spectroscopy to measure the Incident-Photon-to-Current-Efficiency (IPCE). This was conducted by measuring the photo-current resulting from the illumination of the photo-anode sample by monochromated light of various wavelengths. The sample was mounted in a PTFE cell with quartz windows and the electrolyte was 1 M NaOH. The photo-current was measured by chronoamperometry using a potentiostat (Autolab PGSTAT 12) to control the electrode potentials *vs.* an Ag/AgCl reference electrode (Metrohm). The intensity of the monochromated light was assessed with an optical power meter (PM 100, Thorlabs). The resulting IPCE is displayed in Figure 7.8 for both illumination directions and for a number electrode potentials ($E = 1.12, 1.22, 1.32, 1.42 \text{ V vs. RHE}$). As expected, front illumination of Fe_2O_3 results in higher photo-currents than back illumination, which indicates that the mobility of the minority carrier (holes for n-type semiconductor) is limiting.

The photo-current at a given electrode potential can then be predicted from the IPCE through integration. As an example, for AM1.5 light illuminating a cell with optical geometry equal to air-optiwhite-water- Fe_2O_3 -optiwhite-air and a channel width of 1 mm, the predicted photo-current can be seen in Figure 7.9. Note that the IPCE data was interpolated using splines to achieve a smooth result.

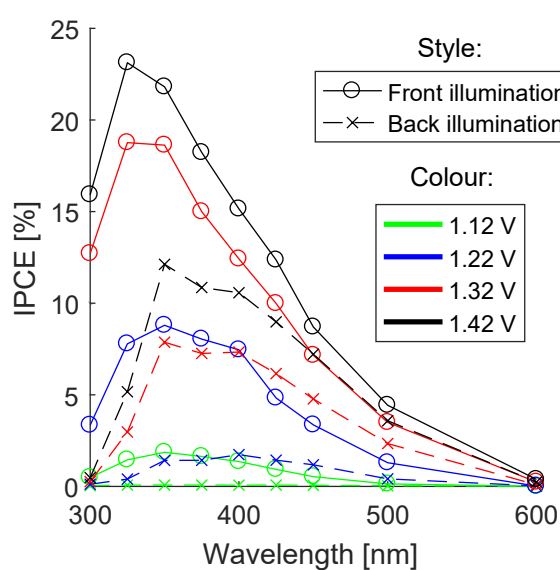


Figure 7.8: The Incident-Photon-to-Current-Efficiency (IPCE) for a front and back illuminated Fe_2O_3 photo-anode at various electrode potentials

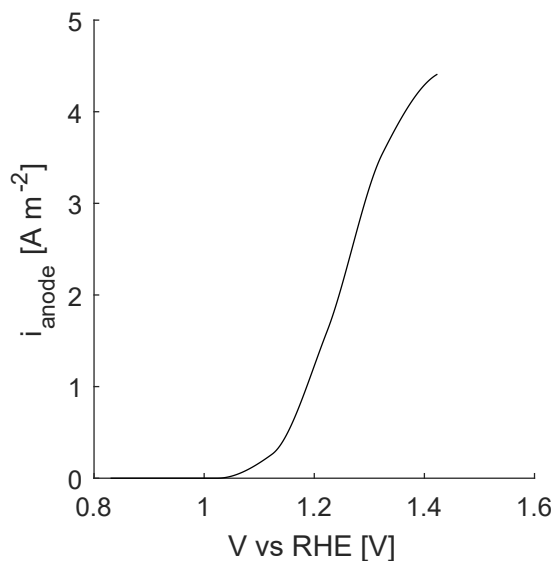


Figure 7.9: Integrated IPCE curve at various electrode potentials for AM1.5 illuminating air-optiwhite-water- Fe_2O_3 -optiwhite-air for a channel width $L_x = 1$ mm

The electrochemical performance of the cathode was determined *via* cyclic voltammetry experiments (Solartron 1280B) on the Pt-FTO samples in 1 M NaOH (against an Ag/AgCl reference electrode). Using the CorrView software, a Butler-Volmer relationship was fitted and the relevant parameters extracted.

The optical properties of the thin film electrodes (Pt-FTO and Fe_2O_3 -FTO), was determined using a custom test cell to ensure that the measurement cell matches the operational environment. Therefore, the test cell was constructed to include an interface between the thin film and the electrolyte and a diagram of the construction is shown in Figure 7.10. The transmittance and total reflectance of the entire test cell was quantified using a UV-vis spectrophotometer with an integrating sphere accessory (Shimadzu UV-2600). To minimise the risk of damage to the spectrophotometer in case of leakage, water was used in the test cell to represent to the ‘electrolyte’ medium, as the optical properties are similar to a 1 M NaOH aqueous solution.

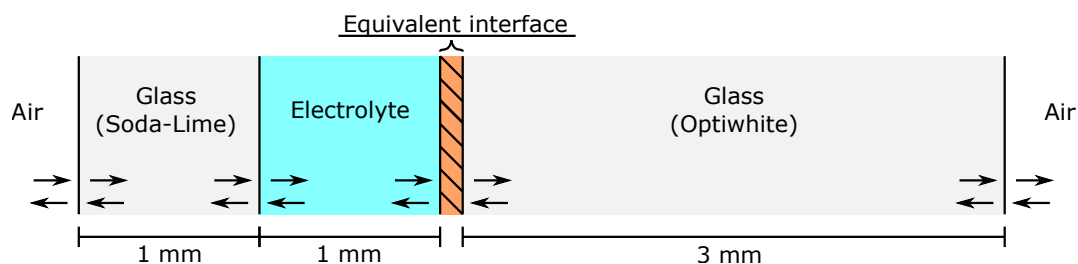
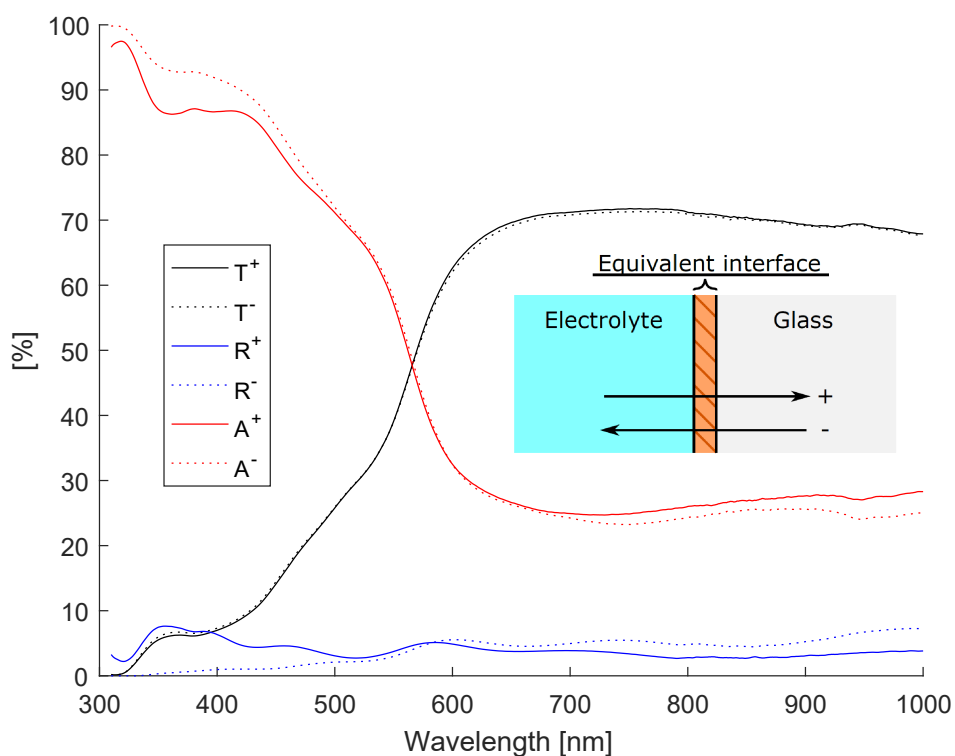


Figure 7.10: Optical geometry of the test cell

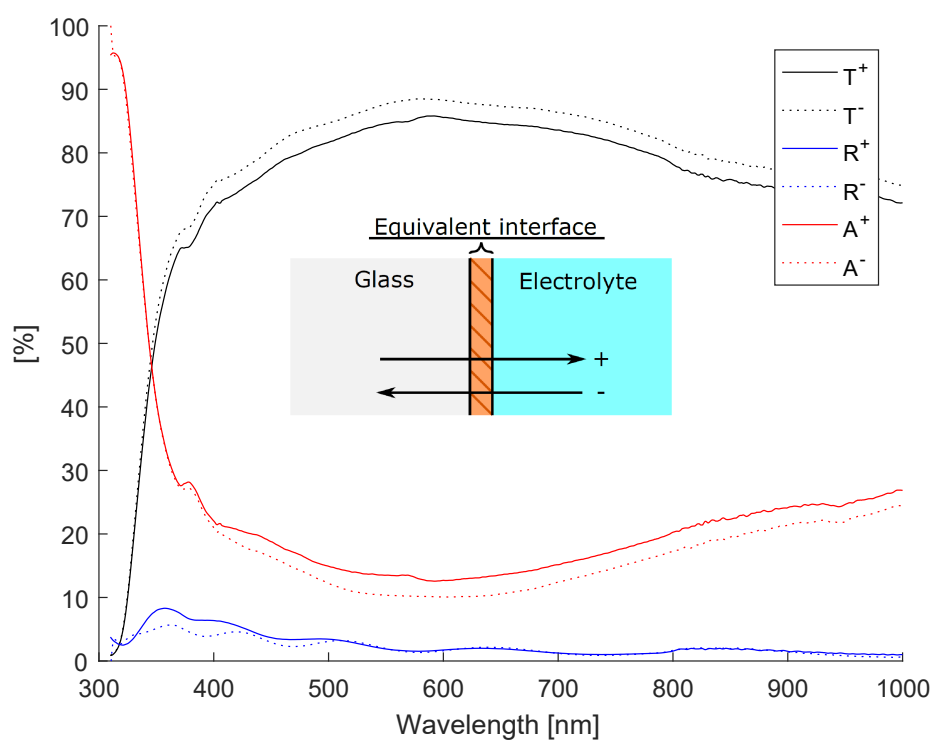
Using the total transmittance and reflectance of the test cell and estimating the optical properties (nk data) of all the components of the cell except for the thin film, the optical properties of the thin film pseudo-interface can be determined for both illumination directions. The method of this inverse calculation is outlined in detail in Appendix 11.5, where the equivalent interface is calculated from the system matrix (calculated from the total transmittance and reflectance) and the inverse matrix of the known layers and interfaces. The resulting transmittance, reflectance and absorptance of the equivalent layers of the photo-anode and cathode thin films are shown in Figure 7.11.

A notable and unrealistic feature of the inferred optical properties of the photo-anode is that at wavelengths lower than 335 nm, the reflectance R^- is negative for light passing glass-photoanode-electrolyte. This is likely due to slight inaccuracies in the estimated refractive index data used for the glass (optiwhite). However, this discrepancy is a very small portion of the entire spectrum and as front illumination is considered, the fraction reflected and hence subject to this error will be small.

All the relevant parameters used for the multiphysics model can be found in Table 7.1, displaying the source of the data.



(a) Photo-anode (Fe₂O₃ on FTO)



(b) Cathode (Pt on FTO)

Figure 7.11: Transmittance, reflectance and absorbance (T , R and A respectively) of the equivalent interface. The superscripts (e.g. R^+ , R^-) denote front and back illumination of the interface as defined by the inset diagram

Table 7.1: Parameters for the full multi-physics model

Parameter		Symbol	Value/Dataset/Notes	Units	Reference
Spectral irradiance		E_λ	AM15 - Direct + Circumsolar	$\text{W m}^{-2} \text{nm}^{-1}$	[55]
Complex refractive index	Air	$\tilde{n}$	-	-	[260]
	Glass	$\tilde{n}$	Optiwhite TM	-	[261]
	Electrolyte	$\tilde{n}$	Assuming water	-	[262]
Equivalent interface	Pt+FTO	$\bar{I}^{equiv}$	See Fig. 7.11b	-	This work
	Fe ₂ O ₃ +FTO	$\bar{I}^{equiv}$	See Fig. 7.11a	-	This work
IPCE	front	η_{IPCE}^f	See Fig. 7.8	-	This work
	back	η_{IPCE}^b	See Fig. 7.8	-	This work
Pt exchange current density		j_o	0.411	A m^{-2}	This work
Pt cathodic charge transfer coefficient		α_c	0.422	-	This work
Pt anodic charge transfer coefficient		α_a	0.288	-	This work
Electrolyte (1 M NaOH) conductivity		κ	16.26	S m^{-1}	[178]
Bias		V_{bias}	1.4	V	-
Diffusivity (in water)	H ₂	D_{H_2}	4.5×10^{-9}	$\text{m}^2 \text{s}^{-1}$	[263]
	O ₂	D_{O_2}	2.1×10^{-9}	$\text{m}^2 \text{s}^{-1}$	[263]
Henry's constant	H ₂	$H_{H_2}^{cp}$	7.7×10^{-6}	$\text{mol m}^{-3} \text{Pa}^{-1}$	[264]
	O ₂	$H_{O_2}^{cp}$	1.3×10^{-5}	$\text{mol m}^{-3} \text{Pa}^{-1}$	[264]
Electrolyte density		ρ	1040	kg m^{-3}	[178]
Electrolyte dynamic viscosity		μ	1.116×10^{-3}	Pa s	[178]

7.5 Results: Constant electrode flux mass transfer model

As previously mentioned, initially a generic mass transfer model, which assumes constant electrode flux, was constructed in order to investigate the relationship between successful product separation and key parameters such as the geometry and electrolyte velocity.

7.5.1 Product separation

In order to determine whether the product cross-over is unacceptable, a mathematical definition of the degree of product cross-over is required. Two equally valid definitions can be made:

1. The collection efficiency η_{coll} is less than some specified amount (Eq. (7.30)). Here, φ_{H_2} is the molar H_2 production rate.

$$\eta_{coll} = \frac{\varphi_{H_2, outlet}^{cathodic\ side}}{\varphi_{H_2}^{cathode}} < 0.99 \quad (7.30)$$

2. The boundary layer crosses centreline (Eq. (7.31)), where the boundary layer is defined as the distance from the surface where the concentration is some specified fraction of the concentration at the surface ($c_{H_2}|_{x=\delta} = c_{H_2}|_{x=surface} \times 0.01$).

$$\delta > L_x/2 \quad (7.31)$$

The definition of product cross-over based on collection efficiency is more commonly discussed in photo-electrochemical water splitting literature and the definition based on boundary layer is more typical of fundamental mass transfer studies. For completeness, both will be considered here.

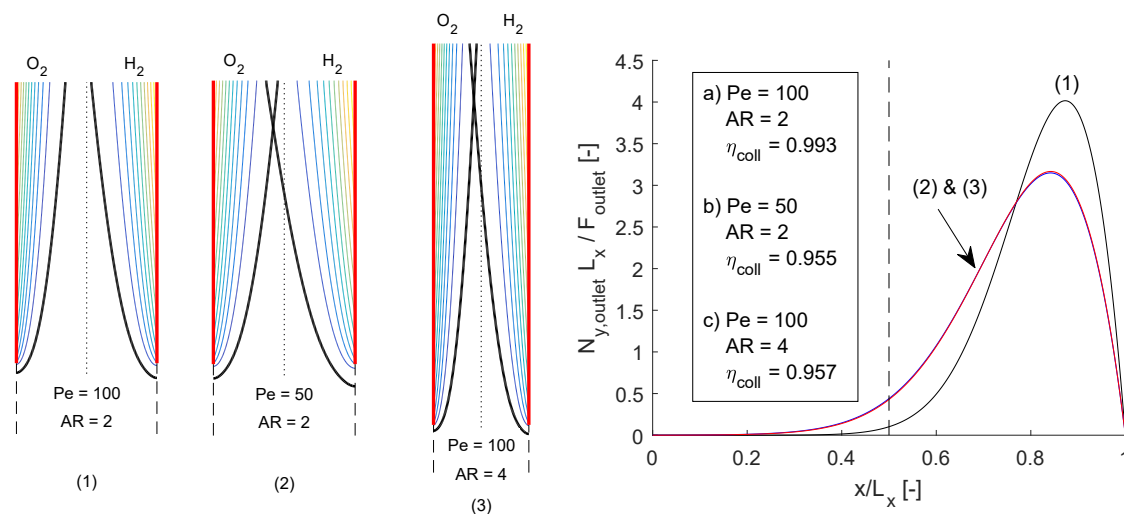
Successful product separation will be determined by the competition between diffusion normal to the electrode surface and convection parallel and this phenomena is described by the dimensionless mass transfer Péclet number.

$$Pe = L_y \langle u_y \rangle / D_x \quad (7.32)$$

It was quickly discovered that along with the mass transfer Péclet number, the geometry was significant in affecting successful product separation. This could be expressed as another dimensionless number: the aspect ratio as given in Eq. (7.33).

$$AR = L_{y, electrode} / L_x \quad (7.33)$$

Examples of three membrane-less cells, with various combinations of the aforementioned dimensionless numbers, are shown in Figure 7.12, where in two of the cases the products cross-over ($Pe = 5$ & $AR = 2$, $Pe = 100$ & $AR = 4$) and one that does not ($Pe = 100$ & $AR = 2$). For the same three cases, the normalised (to facilitate comparison) flux of H_2 at the exit of the reactor is given in Figure 7.12b. It can be observed that the shape of the curves for cases (2)&(3) are identical, which, along with the observation that the ratio of AR to Pe is constant for both cases, indicates that this is likely an important ratio in ascertaining the fundamental behaviour of the cell. Therefore, dimensionless analysis will be used to study this relationship more formally.



(a) Contours showing concentration levels. The bold black contour gives the boundary layer as defined by $c_i|_{x=surface, y=outlet} = 0.01 \times c_i|_{x=surface, y=outlet}$

(b) H_2 flux (normalised against the total molar flowrate per unit channel depth $F_{outlet} = \int N_{y,outlet} dx$) at the outlet of the channel *versus* channel width (normalised against L_x)

Figure 7.12: Example membrane-less cell showing three cases with different values of the Péclet Number (Pe) and the Aspect Ratio (AR)

Furthermore, as shown in 7.12a the hydrogen is the species that ‘crosses over’ to the opposite side of the cell first as the diffusivity of H_2 ($4.5 \times 10^{-9} \text{ m}^2\text{s}^{-1}$) is larger than the diffusivity of O_2 ($2.1 \times 10^{-9} \text{ m}^2\text{s}^{-1}$) [263]. Therefore, as hydrogen will restrict the operational bounds of successful product separation it will be considered exclusively in the following analysis.

7.5.2 Dimensional analysis for constant electrode flux model

Buckingham Pi theorem [265] was used to non-dimensionalise the relevant variables and construct a number so called Pi groups, which will characterise the behaviour of the system. Where possible, the dimensionless groups were chosen to include well-known dimensionless numbers. The Pi groups selected were:

$$\begin{aligned}
\Pi_1 &= \left(\frac{L_y}{L_x} \right) \left(\frac{D_x}{L_x \langle u_y \rangle} \right) = \frac{AR}{Pe} & \Pi_2 &= \frac{D_y}{L_y \langle u_y \rangle} \\
\Pi_3 &= \left(\frac{L_y}{L_x} \right) \left(\frac{R_{i,electrode}}{\rho \langle u_y \rangle} \right) & \Pi_4 &= \frac{\delta}{L_x} \\
\Pi_5 &= \frac{\Delta P}{\rho \langle u_y \rangle^2} & \Pi_6 &= \frac{\rho_i}{\rho} \\
\Pi_7 &= \frac{\mu}{\rho L_x \langle u_y \rangle}
\end{aligned}$$

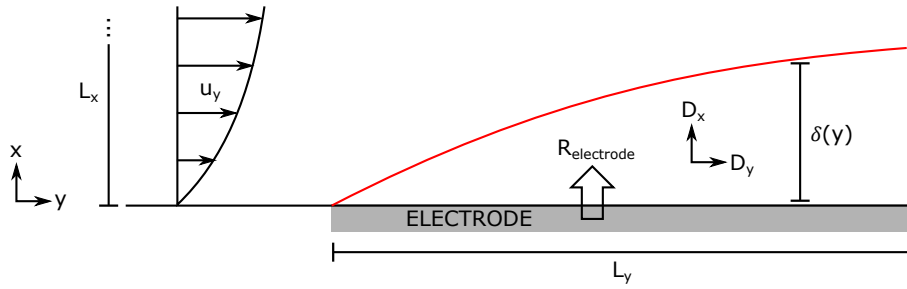


Figure 7.13: Diagram showing the various relevant parameters on the transport of dissolved species away from the electrode surface

A diagram of the system considered for non-dimensionalisation is shown in Figure 7.13. The notation used here is as follows: ΔP_{drop} is pressure drop, D_x/y is the diffusivity in the x or y direction, ρ and ρ_i is the total density and the density of species i , and δ is the boundary layer thickness.

It was established that Π_4 , which contains the boundary layer thickness δ , was only dependent on Π_1 and Π_2 . This means Π_4 was not dependant on Π_3 which contains the reaction rate at the electrode $R_{i,electrode}$, which whilst initially surprising, can be explained by the fact that the definition of the boundary layer thickness δ (and hence Π_4) is the distance at which the concentration is a fraction of the concentration at the surface.

Further rearrangement of the two remaining dimensionless groups (Π_1, Π_2) is obtained though the assumption of isotropic diffusion (*i.e.* $D_x = D_y$). This then means that Π_2 can be expressed as a function of Π_1 as shown in Eq. (7.34), which in turn means that Π_2 can be replaced by AR in the subsequent analysis. This means the behaviour of the membrane-less cell can be conveniently mapped onto a two dimensional plot of AR/Pe *vs.* AR .

$$\Pi_2 = \left(L_x/L_y \right)^2 \Pi_1 \rightarrow \Pi_2 = AR^{-2} \Pi_1 \rightarrow \Pi_2 = f(AR, \Pi_1) \quad (7.34)$$

Figure 7.14, shows the critical value of AR/Pe for a given AR which marks the boundary between successful separation and product cross-over. This is calculated for both definitions of product cross-over (Eq. (7.30) & (7.31)), which demonstrate the approximate equivalence of the two definitions. Three cases are shown with increasingly demanding collection efficiencies η_{coll} , for which the corresponding critical value of AR/Pe is lowered. Such a decrease in AR/Pe could be achieved, for example, by increasing the fluid flow rate. Another noteworthy feature of the results in Figure 7.14, is that the critical AR/Pe tends to a constant for higher aspect ratios, which simplifies the creation of a single simple criterion for product separation as the practical aspect ratio of a membrane-less device is likely to be higher than the point at which the deviation is noticeable ($AR < 2$). Figure 7.15 more clearly shows, for an example of $AR = 10$, that the higher collection efficiencies require a lower AR/Pe in order to ensure no product cross-over.

7.5.3 Bubble formation

The formation of bubbles will have a significant and negative impact on the operation of the membrane-cell. Bubbles will disrupt the smooth laminar flow and this will increase the mass transport of dissolved products to the opposite side of the cell. Consequently, care must be taken to ensure operation outside of bubble forming conditions.

The key driving force in bubble formation is the degree of supersaturation of the dissolved species i (S_i). This is defined in Eq. (7.35) where the equilibrium concentration $c_{i,eq}$ can be calculated using Henry's Law. As the evolving gas bubbles are composed of only one species, the partial pressure will equal the total pressure P and this substitution has been made in Eq. (7.35). Values for the Henry's law constants H^{cp} under standard conditions were taken from literature: 7.7×10^{-6} and 1.3×10^{-5} mol m⁻³ Pa⁻¹ for hydrogen and oxygen respectively [264]. From these values, and the reaction stoichiometry, it can be concluded that hydrogen will reach supersaturation first ($H_{H_2}^{cp} < H_{O_2}^{cp}$) and therefore will be the focus of the following investigation.

$$S_i = \frac{c_i}{c_{i,eq}} \quad c_{i,eq} = H_i^{cp} P \quad (7.35)$$

The relationship between the degree of supersaturation and bubble formation is notoriously difficult to predict as it depends significantly on the experimental conditions, such as the available surface nucleation sites. Therefore, a conservative estimate is used where the critical supersaturation is unity, which is similar to previous work [131].

The concentration of H_2 will be greatest at the outlet and at the surface of the electrode, as the species are formed at the surface and transported to towards the outlet by forced

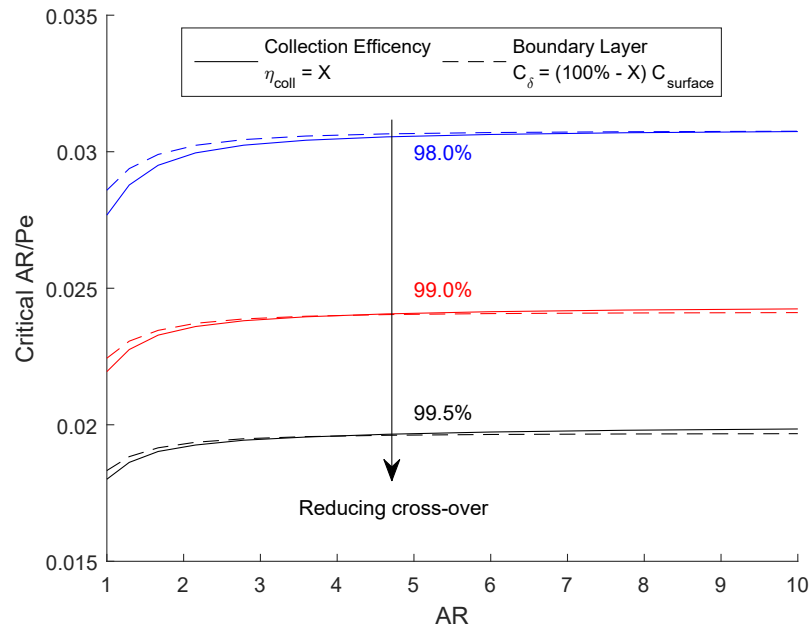


Figure 7.14: The critical AR/Pe for a given AR based on collection efficiency and boundary layer definitions

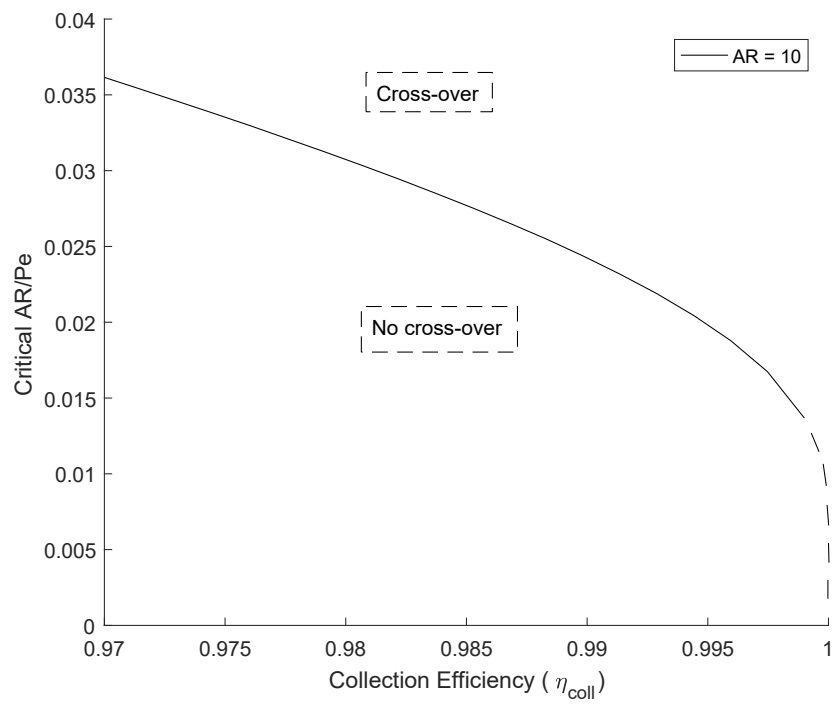


Figure 7.15: Critical AR/Pe against the collection efficiency

convection. Therefore, operation below the critical current density (*i.e.* surface reaction rate) that leads to supersaturation at this point, will ensure that nowhere in the PEC reactor is the electrolyte supersaturated ($S < 1$).

Once more, dimensionless analysis was applied and various dimensionless numbers relevant to bubble formation selected. This introduced a new dimensionless number shown in Eq. (7.36) where $R_{H_2,electrode}$ is the reaction flux at the surface of the electrode.

$$\Pi_R = \frac{R_{H_2,electrode} L_y}{L_x H_{H_2}^{cp} P \langle u_y \rangle} \quad (7.36)$$

This new dimensionless number can be rationalised as the multiplication of the aspect ratio $AR = (L_y/L_x)$ with the ratio of the reaction flux at the surface $R_{H_2,electrode}$ to the convective removal of saturated solution $c_{H_2,eq} \langle u_y \rangle$ where $c_{H_2,eq} = H_{H_2}^{cp} P$. The latter ratio is comparable to a Damköhler number (Da) based on convective transport.

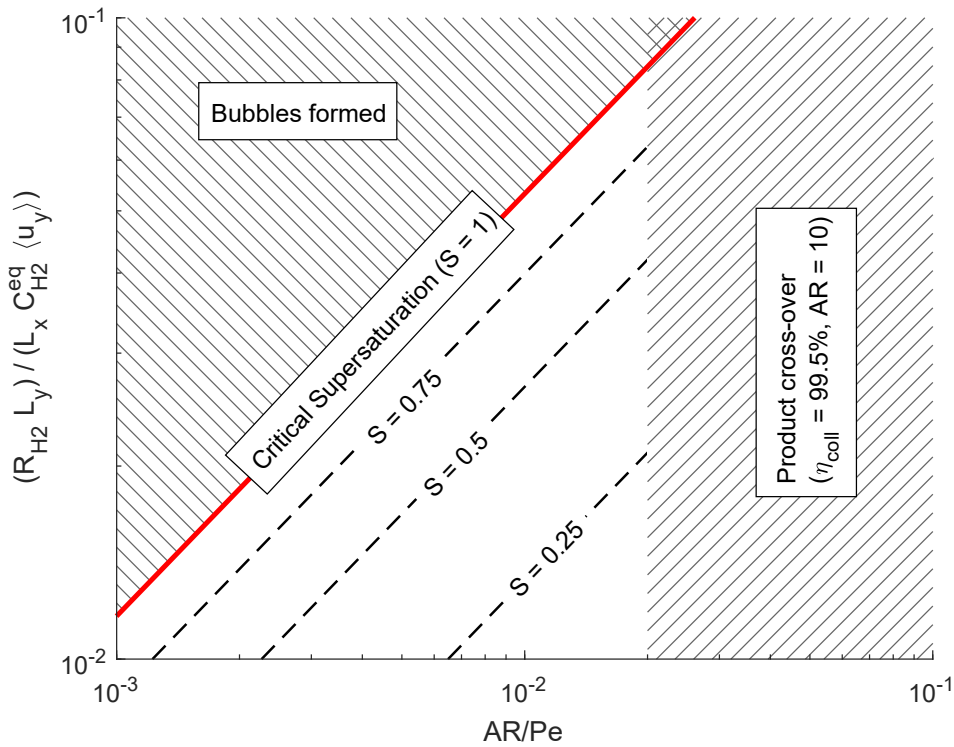


Figure 7.16: Operational design space showing bubble formation and product cross-over regions

It was observed that Π_R was independent of AR , though this independence breaks down as the products cross-over (*i.e.* at the critical value of AR/Pe and AR previously discussed). Thus, a power law was fitted to the relationship between Π_R and AR/Pe and can be seen in AR/Pe Eq. (7.37). Therefore, this information about operation conditions which could lead to undesirable bubble formation can be combined the product cross-separation dimensionless analysis to create one single operational design

space as shown in Figure 7.16. Here, the critical AR/Pe that leads to product cross-over has been specified at a collection efficiency of 99.5%, and an aspect ratio of 10 (cf. Fig. 7.14). This operational design ‘map’ demonstrates the utility of dimensionless analysis as Fig. 7.16 can be used to predict the successful design and operation of any membrane-less PEC reactor which separates products through hydrodynamic control.

$$\left. \frac{R_{i,electrode} L_y}{L_x H_i^{cp} P \langle u_y \rangle} \right|_{S=1} = 1.104 \left(\frac{AR}{Pe} \right)^{0.659} \quad (7.37)$$

For the design map shown in Fig. 7.16, the two critical boundary lines for both bubble formation and product cross-over intercept and this point represents the maximum productivity Π_R for the minimum allowable AR/Pe (e.g. if $\eta_{coll} = 99.5\%$ and $AR = 10$ then $AR/Pe = 0.02$) and the location of this point can be solved for. Taking example values ($D_{H_2} = 4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $H_{H_2}^{cp} = 7.7 \times 10^{-6} \text{ mol m}^{-3} \text{ Pa}^{-1}$ [263, 264]) for the PEC water splitting device described in this chapter, and the assumptions of a faradaic efficiency of unity and that H_2 crosses-over and supersaturates first, Equation (7.38) can be derived which gives the maximum current *versus* the pressure and channel width.

$$j_{max} = 2.802 \times 10^{-08} \left(\frac{P}{L_x} \right) \quad (7.38)$$

Using Eq. (7.38), example values can be input to assess the feasibility of the design. For $L_x = 0.5 \text{ mm}$ and a current density of 80 A m^{-2} (which approximately correlates to a 1 Sun, 10% STH efficiency process [14]), the required pressure is 14.3 bar which appears feasible to design. Equation (7.38) shows that j_{max} is linearly proportional to P and therefore, pressurisation can be used to operate at higher current densities without bubble evolution. An additional method to relax the bubble formation constraint would be to operate a stacked system with multiple photo-electrodes, as the current density for each electrode will be lower. On the subject of operating at higher than atmospheric pressures, it has been mentioned that operation at higher pressures may be beneficial to the overall system as it will reduce the amount of downstream compression required [31, 266].

7.5.4 Separator position in cell

As mention previously, due to the higher diffusivity of hydrogen and the water electrolysis stoichiometry (which means that the molar flux of H_2 is twice that of O_2), the placement of the flow separator (see diagram in Fig. 7.1) at the centreline of the cell may not be the most optimal position. This is investigated here by calculating the

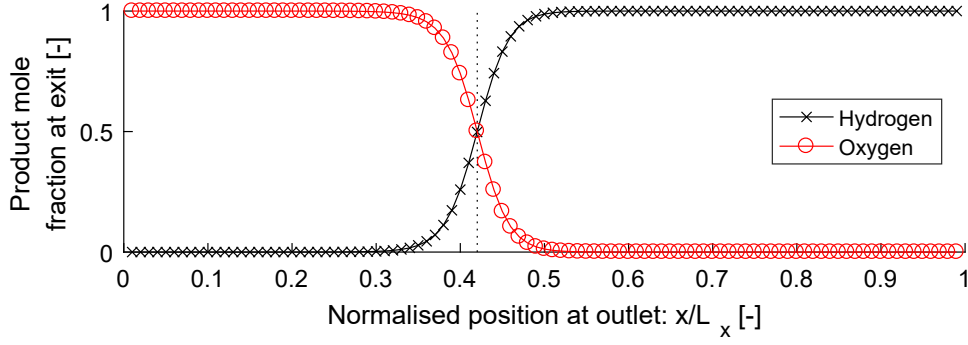


Figure 7.17: Outlet mole fraction of products for $L_x = 5$ mm, $L_{y,electrode} = 10$ mm, $\langle u_y \rangle = 10 \times 10^{-5}$ ms $^{-1}$, $D_{H_2} = 4.5 \times 10^{-9}$ m 2 s $^{-1}$ and $D_{O_2} = 2.1 \times 10^{-9}$ m 2 s $^{-1}$

mole fraction ratio at the outlet of the cell and then the optimal separator position could be found at the intersection of the mole fraction of hydrogen and the oxygen. For a specific case shown in Figure 7.17, where $L_x = 5$ mm, $L_{y,electrode} = 10$ mm and $\langle u_y \rangle = 10 \times 10^{-5}$ ms $^{-1}$, this optimal separator position was found at $x/L_x = 0.420$, which means the cathodic side is 38% wider than the anodic side of the cell.

7.6 Results: Multi-physics model

7.6.1 Current density distribution

From the multi-physics model, the current density distribution for both cathode and anode was calculated considering the electrode kinetics and realistic operational values: $L_x = 1$ mm, $L_y = 10$ mm, $AR/Pe = 0.015$ and $V_{bias} = 1.4$ V. The resulting curve can be seen in Figure 7.18, and shows that the inhomogeneity of current is slightly more for the cathode due to the faster kinetics. That being said the current non-uniformity is negligible: for the cathode the maximum is only 0.07 % above the mean value for the conditions simulated in Figure 7.18. The minimisation of current density distributions in photo-electrochemical cells is important [109], and the membrane-less design described herein performs exemplarily in this regard.

From this example and simulating a range of operational conditions, it can be concluded that the assumption made in the first model of a constant reaction flux at the electrode is accurate. This validates the conclusions drawn such as the operational design map in Figure 7.16.

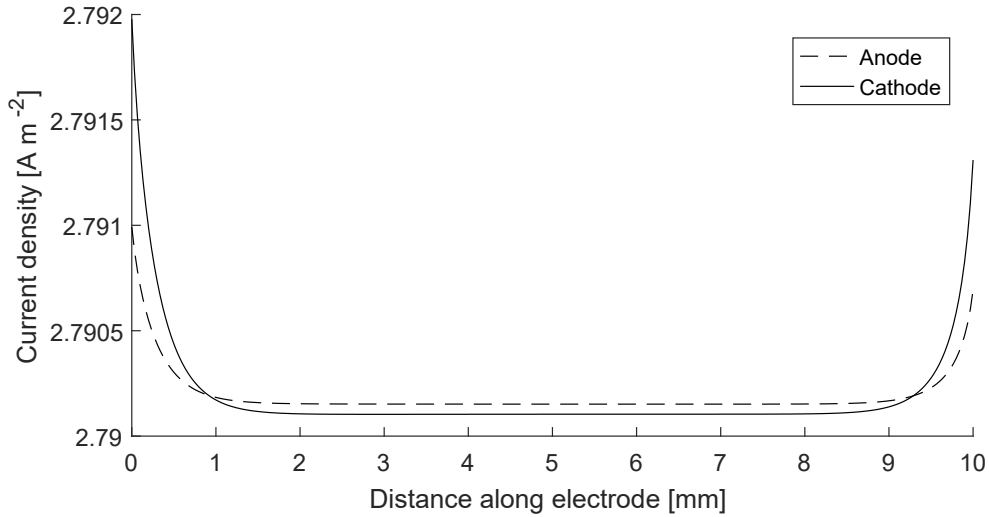


Figure 7.18: Electrode current density from the multiphysics model with $L_x = 1$ mm, $L_{y,electrode} = 10$ mm and $V_{bias} = 1.4$ V

7.6.2 Optical simulation of one unit cell

Using representative complex refractive index data from literature for air, glass, and electrolyte (Table 7.1) and the experimentally calculated equivalent interfaces for the Fe_2O_3 -FTO and Pt-FTO thin films (Fig. 7.11), the optical properties of the unit cell (Fig. 7.7) can be simulated. The results of this simulation for front-side illumination of the photo-anode (*i.e.* light path: glass-cathode-electrolyte-photoanode-glass) is shown in Figure 7.19. This figure shows both the total absorptance and the normalised layer absorption which shows the fraction of light absorbed by a particular layer and wavelength. From this, the parasitic optical losses of the components of the cell can be seen. A wide channel width of $L_x = 5$ mm, was selected in order to more clearly demonstrate the lower wavelength light absorption by the electrolyte. Considering 450 nm wavelength light, approximately 75% of the light absorbed is by the photo-anode ($\text{Fe}_2\text{O}_3 + \text{FTO}$) and the remaining minority absorbed by the platinum nano-particles on the FTO cathode, which could be improved through optimisation of the cell, varying the amount of platinum deposited on the cathode, though this will lead to large cathodic overpotentials. At the same wavelength of 450 nm, the majority of the light is absorbed (total absorbance is approximately 85%), which means that only a small amount of light can pass through to the next cell in a stacked design.

The electrolyte absorption is not significant for a wide bandgap semiconductor such as Fe_2O_3 ($E_g = 2.3$ eV, $\lambda < 540$ nm). Conversely, for a smaller bandgap material such as silicon or germanium, electrolyte absorption may be more critical, which is consistent with work by Döscher *et al.* [120]. This method of optical analysis, with the determination of parasitic absorption, is relatively uncommon for PEC water splitting

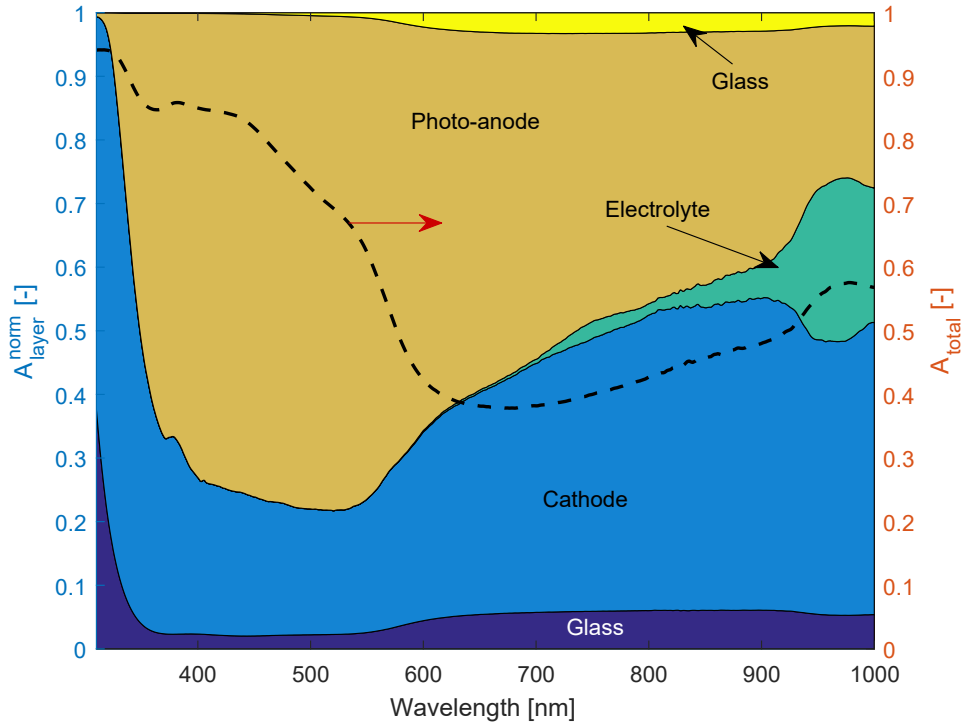


Figure 7.19: The total absorbance and the normalised layer absorption of the example membrane-less photo-electrochemical cell for $L_x = 5$ mm

devices except for a notable example from Cendula *et al.* whom achieved the coherent modelling of the thin films [267] rather than using the equivalent interface method outlined here. This allowed for the prediction of absorption of each individual thin film layer, rather than a lumped absorption model found here.

7.6.3 Optimisation for total energy efficiency

This membrane-less cell design replaces the membrane with forced convective mass transport and both product separation methodologies will incur energy losses. However, in the case of the membrane-less design, this cost of separation is decoupled from the photo-electrode. Therefore, the solar-to-hydrogen efficiency which is used to assess the performance is missing crucial energy inputs, and a more complete system efficiency must be defined. Additionally, for the specific case of a Fe_2O_3 anode, this requires a potential bias which constitutes an energy input which must be accounted for.

Therefore, the definition of Solar-to-Hydrogen (STH) efficiency must be extending to include energy input additional to the solar power, and an overall system efficiency or the total input Energy to Hydrogen Efficiency (ETH) must be used. Given in Eq. (7.39), this system efficiency is similar to the "general expression efficiency" outlined by Coridan *et al.* [58].

$$\eta_{ETH} = \frac{\varphi_{H_2} G_{f,H_2}^0}{P_{pump} + P_{solar} + P_{bias}} \quad (7.39)$$

Now a suitable efficiency is defined, the interaction between operational conditions and efficiency can be investigated. For example, there are many phenomena which may be in competition when optimising for the total energy efficiency such as the energetic requirements of pumping, separation of products, electrolyte parasitic absorptance and ohmic solution losses. Assuming a reasonable pump efficiency $\eta_{pump} \approx 0.6$, the required pumping power can be found in Eq. (7.40) [268].

$$P_{pump} = \frac{\dot{Q} \Delta P_{drop}}{\eta_{pump}} \quad (7.40)$$

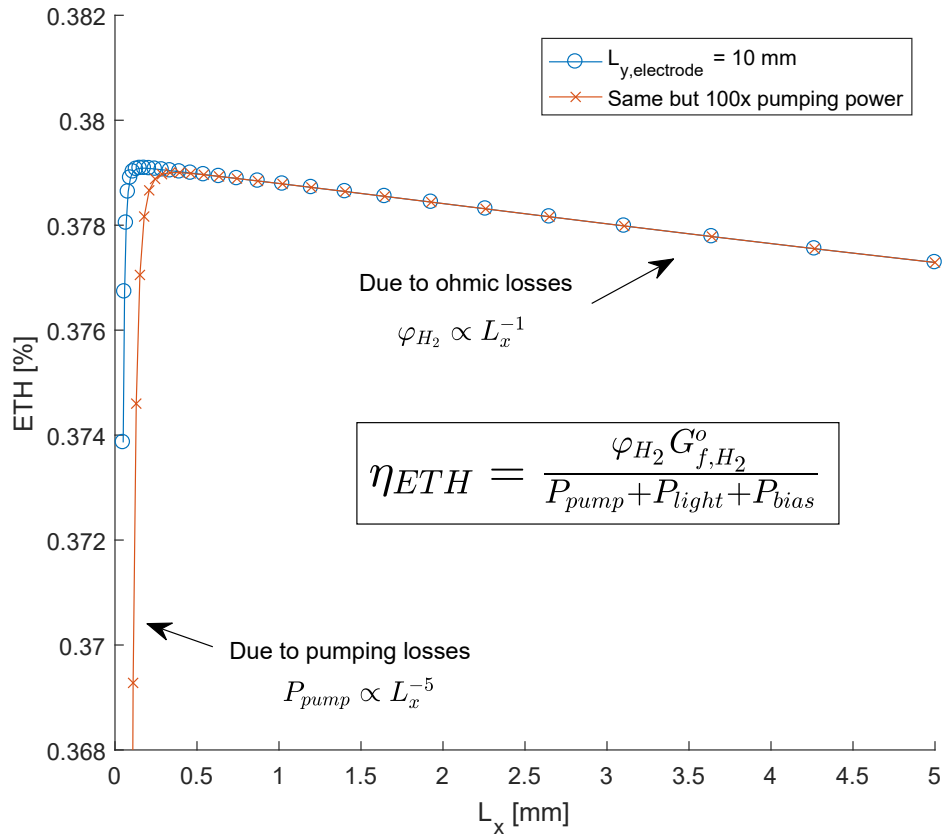


Figure 7.20: Sensitivity of system efficiency to channel width (L_x)

The effect of the channel width L_x on the total input Energy-To-Hydrogen efficiency is plotted in Figure 7.20 for an $AR/Pe = 0.015$ to ensure product separation and an electrode length $L_{y,electrode} = 10 \text{ mm}$.

At smaller channel widths, the ETH efficiency was constrained by pumping power required and this was confirmed by increasing the pumping power 100 fold and observing the results. At larger channel widths, the efficiency will be constrained by the

electrolyte ohmic losses and parasitic absorptance. However, as the selected semiconductor has a wide bandgap, the parasitic absorption in the electrolyte is very small (see Fig. 7.19) and hence a linear dependence of ETH against L_x is observed. This infers that ohmic losses in the electrolyte dominate as ohmic losses scale linearly with distance and optical losses would scale exponentially. Consequently, Figure 7.19 shows that a larger than optimum channel width does not negatively impact the efficiency significantly and this may make manufacture easier as larger channel widths can be tolerated.

It is important to point out that the low efficiency shown in Fig. 7.20 does not originate from the fundamental design of the reactor, but the sub-optimal properties of the semiconductor. With better materials, fabrication methods and device designs which are unbiased (*e.g.* multi-junction systems), this membrane-less reactor design could realise far higher efficiencies than simulated here.

7.6.4 Theoretical evaluation of stacked design

The model can be used to evaluate of stacked design for the case study based on experimental data taken from a Fe_2O_3 photo-anode. The efficiency gains made through stacking the cells, where light that passes through any cell can be absorbed by the subsequent cell, can be seen in Figure 7.21. The improvements demonstrated here are small since the transmittance of above bandgap photons is low. It is possible to imagine a more impressive improvement in efficiency with photo-electrodes which have a higher transmittance, and a high absorbed photon to current efficiency [250, 251].

There have been a number of experimental demonstrations where stacked photo-electrochemical interfaces are used [81, 82, 250, 251]. Notably, Kim *et al.* [81] used two photo-anodes of different bandgaps (BiVO_4 and Fe_2O_3) in order to efficiently capture more of the light spectrum and achieved 7.7 % unbiased STH efficiency by coupling with a silicon solar cell. This methodology is the photo-electrochemical equivalent to multi-junction system, with the difference that the photo-electrodes are electrically in parallel and optically in series (see Chapter 3 for a discussion on conceptual device configuration).

7.7 Prospective future work

Future work could include the investigation of the relationship between the photo-electrode properties (*i.e.* film thickness) and stacked design efficiency. This design

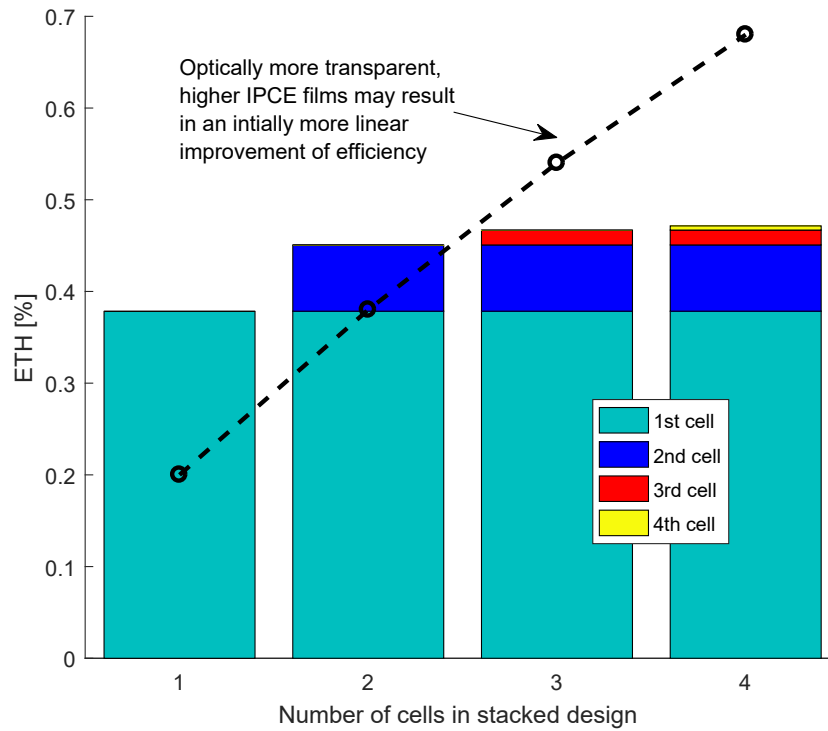


Figure 7.21: Example efficiency gains with multiple cells stacked up showing the individual contribution of each cell to the total Energy-To-Hydrogen efficiency (η_{ETH}) of the whole stack

could then potentially realise high efficiencies without the need for nanostructuring with materials which have an unfavourable path length to absorption length.

Further study is required in order to understand the systems level design required to operate a membrane-less cell. For example, this analysis does not consider the downstream dissolved gas removal from electrolyte which will be required. This could be achieved through the reduction in pressure, an increase in temperature, or through sparging (though this will then require another separation step). A full investigation into the technical and economics feasibility of dissolved gas removal methods would be required in order to demonstrate the scalability of this design.

7.8 Conclusions

- A novel membrane-less photo-electrochemical reactor design is outlined which separates the dissolved hydrogen and oxygen *via* forced convection.
- This reactor design removes the membrane and reduces the ohmic pathlength which leads to a significant reduction in the required photo-voltage which relaxes the requirements on the semiconductor.
- This design lends itself well to stacking of multiple PEC cells which would allow

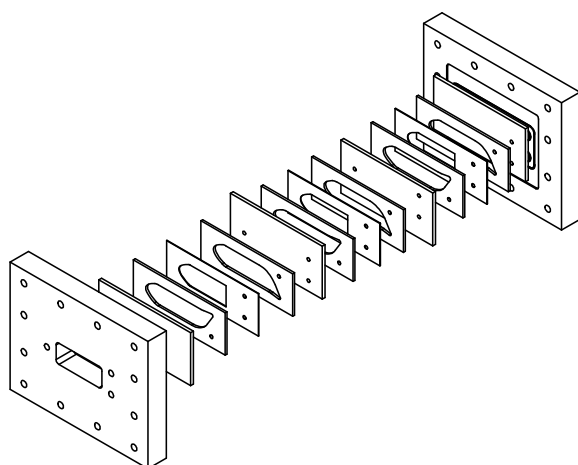
above bandgap photons to be absorbed in sequential semiconductor-electrolyte interfaces. This would relax the typical compromise between the path length of charge carriers and the absorption length of the semiconductor for metal oxide photo-electrodes. This could be a methodology for realising higher efficiency with these materials.

- A constant electrode flux mass transfer model was created in order to perform dimensionless analysis to obtain a fundamental understanding of the operational parameters and design which influences the performance of the reactor (*i.e.* product separation, bubble suppression). The following dimensionless numbers were found to influence this performance: aspect ratio (AR), aspect ratio divided by Péclet number (AR/Pe), and a term pertaining to the rate of reaction at the surface, the geometry and the rate of removal of saturated solution ($R_{H_2}L_y/L_xH_{H_2}^{cp}P\langle u_y \rangle$). This analysis permits the prediction of successful operation regimes.
- A multi-physics model was set up, which included the optics (transfer matrix method), the electrolyte charge transport (secondary current density distribution) and a mass transfer model of dissolved products. Using experimental data from Fe_2O_3 as a case study, the results from the multi-physics model were used to validate the conclusions from the constant flux mass transfer model which was used for the dimensionless analysis. A negligible current density distribution was theoretically shown, and the parasitic optical losses discussed.
- For example experimental data, the total efficiency increase upon stacking of membrane-less cells was small as the optical properties of the semiconductor film were not optimised for this configuration. It does, however, demonstrate the potential efficiency gain upon stacking with a high APCE but low IPCE film. This was compared with experimental demonstrations of optically stacked photo-electrochemical interfaces.
- In this chapter, it is demonstrated that product separation is theoretically feasible which allows for the removal of the membrane and its associated energetic losses, and for the achievement of a stacked photo-electrochemical design where light can be absorbed by multiple photo-electrode.

Chapter 8

Membrane-less PEC: Preliminary experimental results

An experimental apparatus was built in order to test the membrane-less PEC design outlined in the preceding Chapter. The promising preliminary results are discussed, whilst highlighting the present deficiencies in the experimental method and discussing improvements for future work. The achieved collection efficiency of $\sim 90\%$ is a step towards the complete separation of products in an efficient PEC design which could realise the advantages of stacked architectures.



8.1 Introduction

To build on our previous published work [1] and the previous chapter, a experimental prototype of the membrane-less reactor design was fabricated.

The key figure of merit for the preliminary experiments, is the collection (or separation) efficiency defined in Eq. (8.1) where φ_{H_2} is the molar production rate of hydrogen. This ratio must be as large as possible to ensure the product cross-over does not lead to safety issues and a decrease in the faradaic efficiency.

$$\eta_{coll} = \frac{\varphi_{H_2, outlet}^{cathodic\ side}}{\varphi_{H_2}^{cathode}} \quad (8.1)$$

8.2 Design of PEC reactor

The design of the membrane-less reactor is shown in Figure 8.1 and is constructed with the type of fluid manifold design commonly seen in fuels cells or flat-plate heat exchangers. It comprises of two end clamping plates made of PVC, between which the electrode assembly is clamped. Each unit cell comprises of a cathode plate, a cathodic chamber gasket, a flow separator, an anodic side gasket, and finally the anode. The laser-cut gaskets silicone gaskets direct the electrolyte flow to the reactor exits. Two sets of gaskets were made with different thickness (0.5 or 1 mm) in order to adjust the distance between electrodes. The flow separator splits the flow into two parts and is made of stainless steel to minimise corrosion. Each electrode is made from 5×10 cm FTO coated glass with inlet and outlet holes drilled through. Electrical connection to the FTO is made using silver epoxy in the location shown in Fig. 8.1. A photograph of half of the reactor (with one cell) is shown in Figure 8.2.

Initially, the electrode area was demarcated by applying a thin layer of epoxy to the surface of the FTO using a doctor blade approach, whilst masking the electrode area ($1 \text{ cm} \times 4 \text{ cm}$) with tape. Once the epoxy had set, the tape was removed and the exposed FTO surface cleaned with ethanol and water. One of the resulting electrodes can be seen in Fig. 8.2. As explained later, this method was then superseded by only depositing Pt nanoparticles on the desired electrode area and leaving the remaining electrode uncovered. The Pt deposition steps are as follows: FTO was cleaned in acetone and DI water before being thoroughly dried. Then, $1 \mu\text{L}$ of 0.01 M solution of $\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in EtOH, is drop cast onto the FTO substrate, using tape as a mask. Once dry, the tape was removed and the sample was heated at 385°C for 15 minutes.

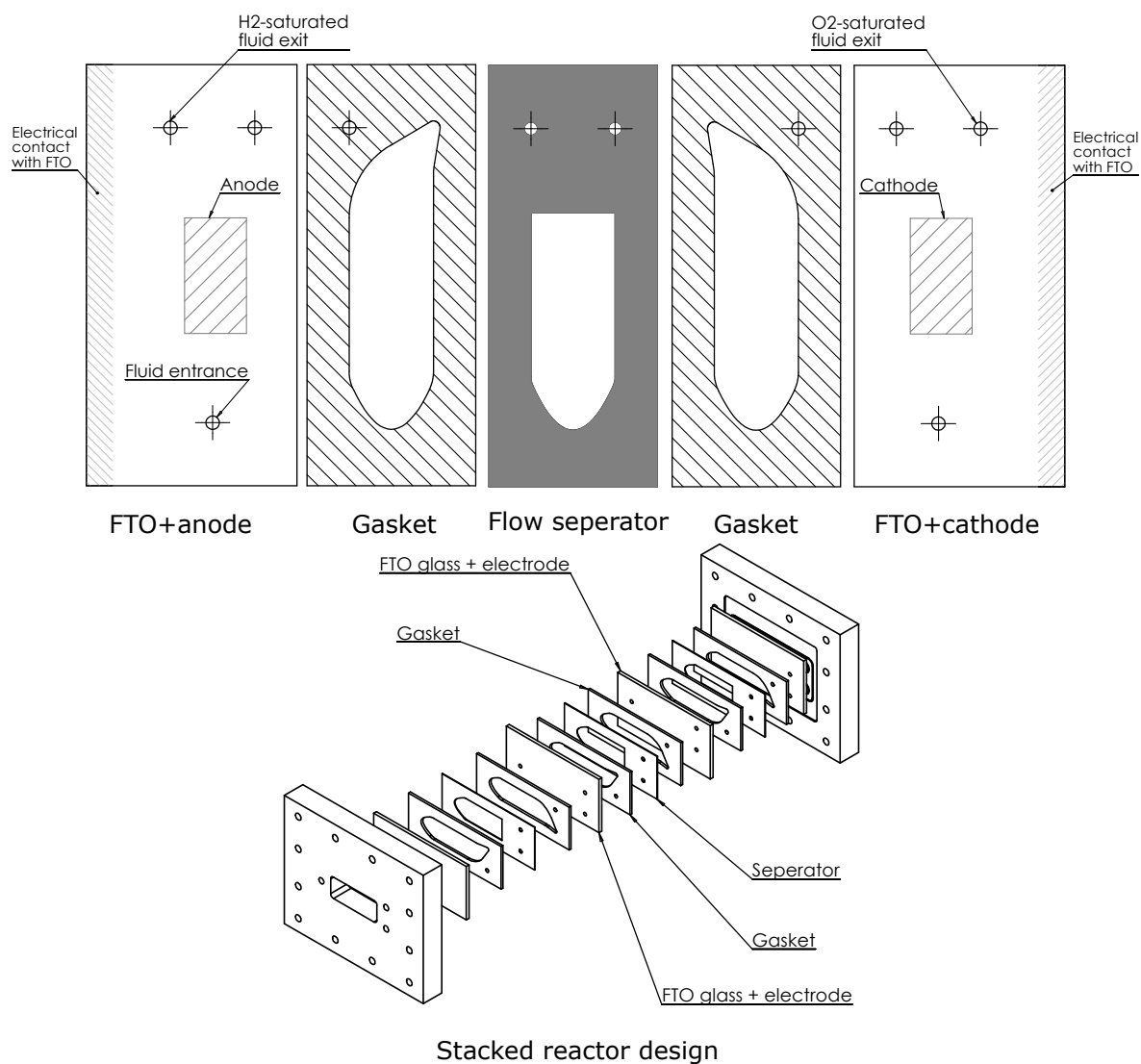


Figure 8.1: CAD diagram of stacked reactor design

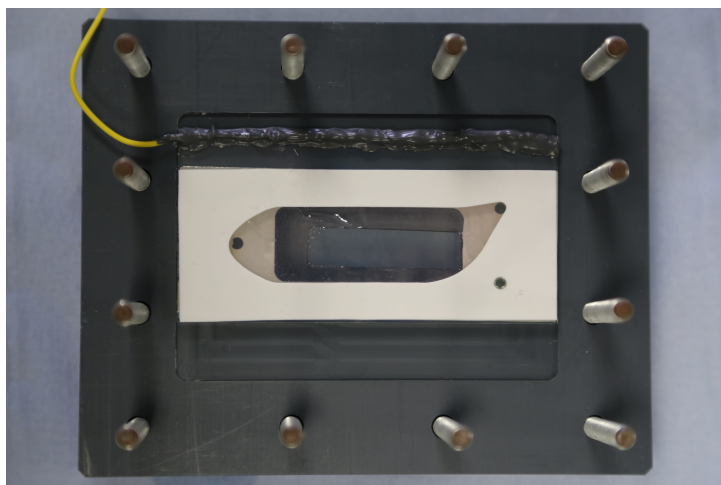


Figure 8.2: Photograph of the disassembled membrane-less reactor showing half of the unit electrochemical cell

8.3 Experimental set-up and methodology

As the quantification of the dissolved hydrogen concentration is key to the determination of the collection efficiency η_{coll} , the set-up of the experiment was designed around the detection method. Therefore, the hydrogen detection methodology is described first.

8.3.1 Hydrogen detection

Accurate and real time measurement of the dissolved H_2 proved challenging and a number of different methods were tested, some of which are shown in Figure 8.3. The ideal H_2 sensor would be repeatable, have a fast response time and be insensitive to flow so as to facilitate in-situ measurements which, therefore, suits an electrochemical method: amperometric detection.

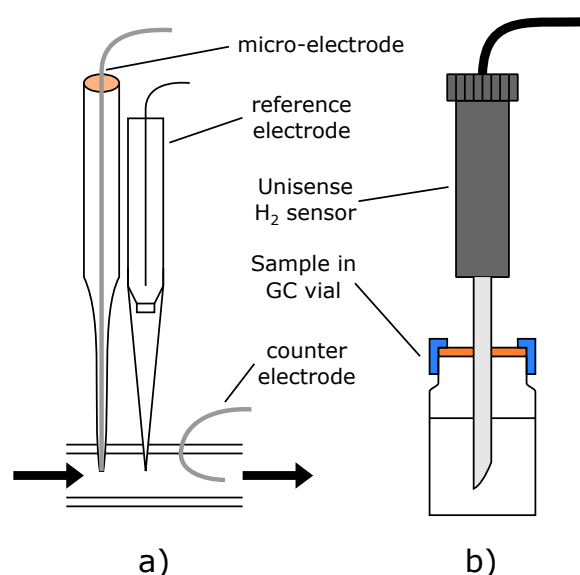


Figure 8.3: H_2 detection methods. a) home made micro-electrode *vs.* reference electrode
b) commercial H_2 Clark-type microsensor

Initially, lab built H_2 detection methods were attempted using a home made open source potentiostat (DStat) in order accurately measure the small detection currents ($\sim nA - \mu A$). More details on the DStat potentiostat are outlined in Appendix 11.2. An electrochemical detector normally used for HPLC detection was tested with H_2 saturated water and it was found that it was only sensitive at neutral pHs. Under the alkaline conditions used in the membrane-less reactor, the H_2 signal to noise ratio became untenable, potentially due to corrosion reactions occurring within the cell (stainless steel reactor body).

Next, a custom made three probe amperometric detection cell was made consisting of a working electrode, an Ag/AgCl reference electrode, and a platinum wire counter electrode. Two types of working electrodes were used: 1) a custom made micro-electrodes, made from ‘pulling’ a capillary glass tube containing a thin Pt wire over a heat source, and then polishing the tip to reveal an electrode area. 2) a commercially available Pt screen-printed electrode (MicruX Technologies) upon which a catalytic layer of Pt black was deposited. Ultimately, whilst the home made sensors were very responsive to low concentrations of H₂ and could be placed inline at the reactor outlet, the repeatability of measurements was a clear issue.

Ultimately, a commercial H₂ microsensor (Unisense H2-NP) that operated on the same principles as O₂ Clarke electrode was borrowed temporarily in order to obtain preliminary results. As the signal was unstable when the electrolyte was flowing, the measurement was constrained to taking aliquots and then separately measuring the H₂ concentration under stagnant conditions. The sensors were non-standard and had been customised by the manufacturer in order to accommodate a larger piercing needle tip.

Calibration of Unisense H₂ sensor

As the H₂ sensor response is linear, it only requires a two point calibration and was achieved by measuring 0.1 M NaOH aqueous solutions of two different known H₂ concentrations. The first contained no dissolved H₂ and the second was made by bubbling 3.24 and 37.0 ml min⁻¹ of H₂ and Ar respectively through *ca.* 100 ml 0.1 M NaOH for 1 hours. By assuming a Henry’s constant of $7.7 \times 10^{-6} \text{ mol m}^{-3} \text{ Pa}$ [264] and equilibrium is reached, this results in a 0.81 % molar percentage of saturated solution at room temperature. The concentration of hydrogen could then be deduced from: $c_{\text{H}_2} [\text{mol m}^{-3}] = 7.82 \times 10^{-5} \times (\text{Signal} [\text{mV}] - 3.82)$.

8.3.2 Experimental apparatus

The diagram of the set-up can be found in Figure 8.4. Firstly, fresh electrolyte is supplied by either a gravity fed system or a peristaltic pump from a storage bottle. The gravity fed system utilised the principles of a Mariotte’s bottle which delivers a fixed head pressure independent on the level of the electrolyte in the bottle. The electrolyte then flows through PEC device and is split into two streams: anodic side and cathodic side streams. Both streams then pass through an adjustable tube clamp which allows fine adjustment to ensure the PEC device output flowrates were equal. Then, both streams are delivered to two pipettes which were used for flowrate measurement by measuring volume against time elapsed manually. When samples of the electrolyte are

to be taken, a GC vial is used to collect the flowing electrolyte immediately before the flow measurement apparatus.

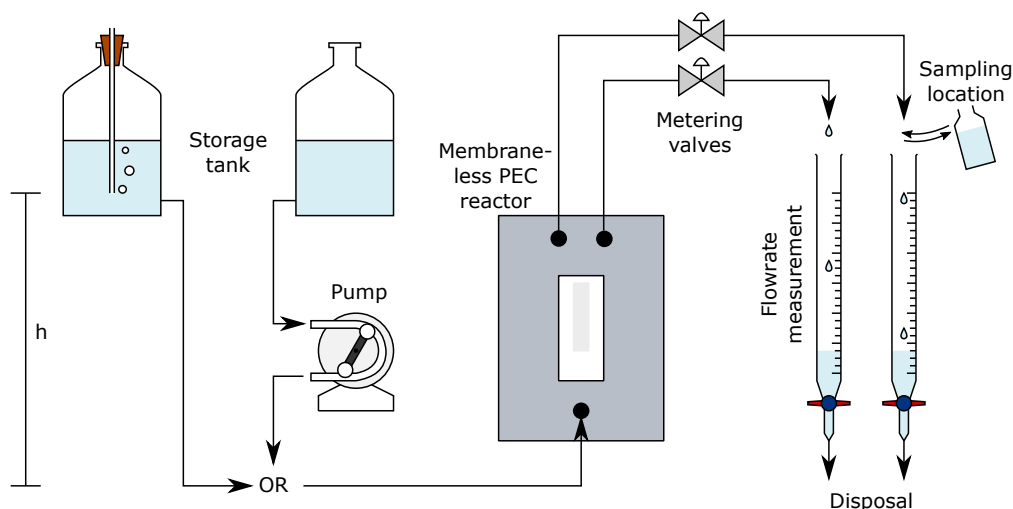


Figure 8.4: Diagram of membrane-less PEC device testing

8.3.3 Experimental methodology

The experiment was conducted by first fixing the inlet flowrate and adjusting the tube clamps which acted as metering valves to ensure an equal flowrate through each. Then, the current was passed through the membrane-less device galvanostatically. Periodically, samples were collected into 2 ml GC vials simultaneously from both streams. Finally, the samples are measured sequentially using the H_2 sensor with as little delay as possible in order to reduce the H_2 lost to the surrounding.

8.4 Preliminary experimental results

8.4.1 First experimental iteration

The first experiments were conducted using a thin layer of epoxy to mask out the area of the electrochemical interface. The resulting H_2 concentration from operating the PEC cell with 1 mm gaskets and at a total electrolyte flowrate of 5.8 ml min^{-2} can be seen in Figure 8.5 for three applied current densities. Immediately, two issues with the experiment were observed. Firstly, it takes a significant amount of current before H_2 is detected. Secondly, the required electric potential between electrodes in order to sustain the current is undesirable large (*e.g* 3+ V). At these potentials FTO will not be stable in NaOH and will be reduced to tin. This is then likely the main cause of the ‘missing’ H_2 .

A third and final issue revealed itself upon inspection of the dismantled PEC cell. Over the course of the experiments (3 days) the epoxy mask swelled and wrinkled, so disrupting the flow through the cell and exposing unwanted electrode area. This flow disruption was reflected in the calculated separation efficiency worsening which prompted the inspection of the electrodes.

Despite these issues, the separation system still showed a separation efficiency of 87.2 % at 400 μA which establishes that the device can separate dissolved H_2 and O_2 but not yet to a degree which could be considered safe to scale up.

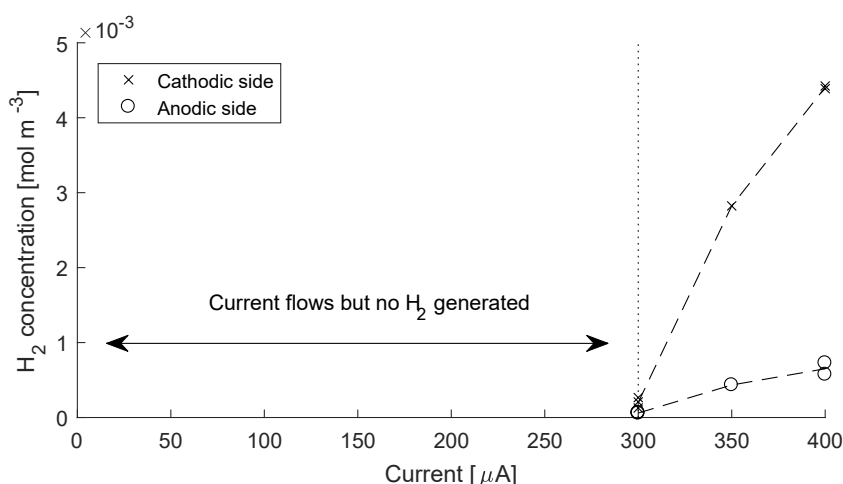


Figure 8.5: The measured H_2 concentration of anodic and cathodic electrolyte streams *versus* various applied current. The total flowrate was 5.8 ml min^{-1} and 1 mm thick gaskets were used

8.4.2 Second experimental iteration

In order to reduce or circumvent a number of issues in the first iteration of experiments, a number of changes were made. Firstly, the epoxy mask was removed and Pt nanoparticles were deposited in a rectangular area (4 cm^2) by masking with transparent adhesive tape. Additionally, the gravity feed system was replaced with a peristaltic pump in order to maintain a constant flow rate over many hours. Whilst the Mariotte's bottle maintained a constant head pressure, it was found the flowrate was very susceptible to accidental movements of any piping and was therefore challenging to obtain a specific flowrate. The pump, however, introduced flowrate fluctuations on each rotation of the rotor assembly. This effect was successfully reduced by a home-made pulsation damper, consisting of a 50 ml syringe filled with air connected at a 3-way junction at the outlet of the pump, where the compressible nature of the air damped the oscillations.

These results showed an improved separation efficiency and were tested to higher current densities, as the overpotentials were lowered with the improved catalysis which

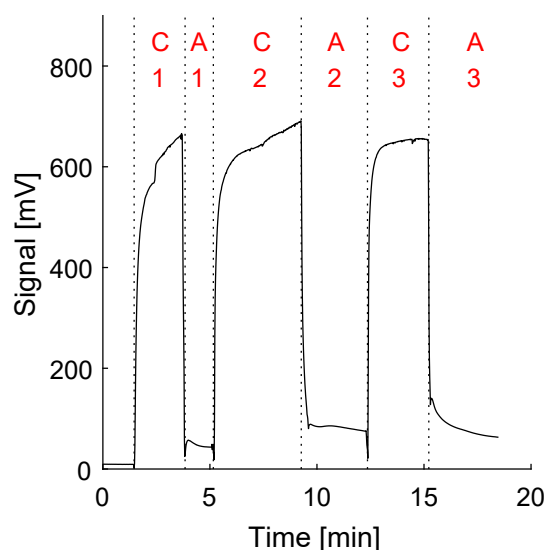


Figure 8.6: H_2 detector responses for 3 different samples (20 ml min^{-1} total flowrate, 5 mA applied) where C is the cathodic side stream, and A is the anodic side stream.

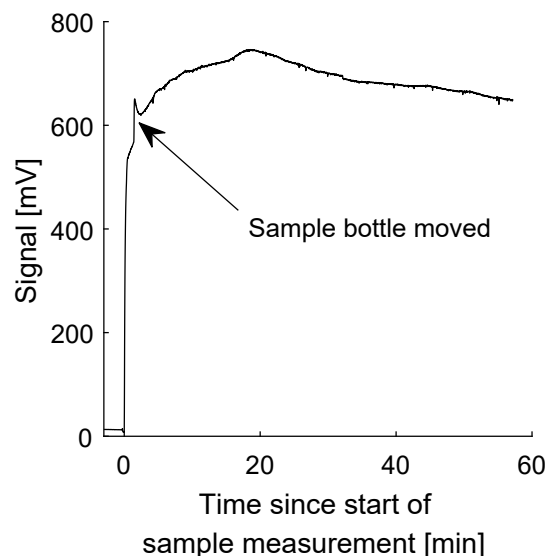


Figure 8.7: Long term response of the H_2 detector to an example electrolyte sample which demonstrates the undesirably long measurement timescale.

significantly reduced the voltage required. A total flowrate of 20 ml min^{-1} was used with an applied current of 5 mA . Assuming the catalyst area is the electrode area, the current density of 1.25 mA cm^{-2} corresponds to approximately 1.54% STH efficiency under 1 Sun.

Figure 8.6 shows the raw data from the H_2 sensor for three pairs of samples, using gaskets of thickness 1 mm . The samples were taken from the membrane-less PEC reactor at approximately 6 minute intervals. The calculated average separation efficiency for the three samples is then 92.7 % and the average faradaic efficiency is 71.8 % which is improved from the first experiment iteration. Reducing the gasket thickness to 0.5 mm , resulted in a separation efficiency of 91.3 % and a faradaic efficiency of 82.1 % under the same experimental conditions. Caution must be taken as there are likely large errors in these values due to the suboptimal performance of the H_2 measurement methodology. However, this clearly demonstrates H_2 can be separated *via* a hydrodynamic flow field, and further work will be required to push the separation efficiency closer to unity.

8.4.3 Remaining issues and future work

The first and foremost remaining issue with the experimental apparatus is the aforementioned difficulties in dissolved H_2 detection. As demonstrated by Figure 8.7, the detection time is too sluggish when samples are collected and measured in stagnant aliquots. This is significantly less responsive than the manufacturer's specifications but this disparity potentially could have been due to the non-standard needle tip used. The

batch sampling methodology effectively slows down the sampling rate of the reactor to a sample every ~ 5 minutes. Fast in-situ analysis would allow the examination of reactor dynamics and operability.

Furthermore, detection of the gases immediately after exiting the PEC reactor would reduce the time available for gas desorption from the electrolyte. This inaccuracy could actually improve the measured collection efficiency as the greater the concentration gradient, the faster the desorption of dissolved gases. Consequently, it is expected that the cathodic side sample will lose H_2 faster than the anodic side sample and therefore faster detection may increase the amount of cathodic side H_2 .

The final remaining issue is that ensuring an exactly equal flowrate at the reactor exit using the adjustable tube clamps was a laborious task and these valves should be replaced to obtain finer control of the flowrate.

Clearly, this work is ongoing and future work should include:

- To improve the collection efficiency to $\eta_{coll} > 0.99$ and to realise the efficiency gains possible through stacked architectures
- To determine whether bubble suppression is possible over a long time frame (*e.g.* a day) and to measure the long term stability of the separation efficiency
- Investigate the downstream removal of dissolved products from electrolyte both experimentally and economically
- Conduct a parameter study varying flowrate, current applied, electrode dimensions and channel width to observe the effect on separation efficiency, bubble suppression and the predicted overall energy to hydrogen efficiency
- Compare results with the theoretical simulations outlined in Chapter 7

8.5 Conclusions

- An experimental set-up was designed to test the concept of dissolved gas separation through forced convection and separation efficiencies of up to *ca.* 90% are demonstrated.
- Whilst a very promising start, the product cross-over empirically measured here does not yet meet safety requirements and further work will be required to demonstrate that such a design is technologically possible.
- In order to successfully validate the model and the operability of the membraneless design, a dissolved H_2 sensor that can measure the output concentration in real-time, in-situ is required.

Chapter 9

Conclusions and future work proposal

9.1 Conclusions

This thesis focused on the photo-electrochemical engineering of solar water splitting devices and is arranged as follows: Firstly, an introduction is given to the challenges emerging in meeting human consumption of energy sustainably (Chapter 1) and one potential route to a sustainable fuel derived from the conversion of solar energy, *i.e.* photo-electrochemical water splitting, is outlined (Chapter 2). The thermodynamics of photo-electrochemical water splitting is revisited in Chapter 3, and generalised framework for calculating the thermodynamic limiting efficiency is given, permitting the investigating of a number of understudied configurations. Chapter 4 explores the obstacles to designing a ‘perfect’ photo-electrochemical water splitting device, with a critical analysis of selected scalable reactor designs found in literature. Chapter 5 and 6 both deal with two engineering issues arising from the analysis in Chapter 4. Firstly, the relationship between the bubbles evolved on the surface of a photo-electrode and the detrimental light scattering from these bubbles. Secondly, the resistive losses in a common substrate, fluorine doped tin oxide, was quantified through numerical simulation for various electrode dimensions. Chapter 7 and 8 focuses on membrane-less PEC reactor design which uses laminar forced convection as a means of product separation of dissolved gases. This design is studied theoretically (Chapter 7) and preliminary experimental results are given in Chapter 8. The main conclusions from each of the chapters will now be summarised.

A limiting efficiency calculation tool was developed (etaPEC released under an open source licence) which unifies and extends previous work. This allows for the investigation into the limiting efficiency and optimal bandgap of unorthodox PEC architectures and permutations of conceptual PEC design. This tool also facilitated the comparison of a number of experimental results with the limiting efficiency of that configuration.

The design of PEC reactors is systematically deconstructed to the fundamental challenges and the often competing design goals. From this, it is clear that designing a scalable PEC reactor is incredibly complicated, although not impossible. A literature review of reactor designs shows the increasing interest in engineering of PEC devices and the progress made in the last couple of years.

For high efficiency device, optical losses due to light scattering from bubbles evolving at the electrochemical surface will negatively impact performance. For case study of a fluorine doped tin oxide electrode, the optical losses were quantified ($\sim 5\%$ for 8 mA cm^{-2}) and given the small area of the sample (2.25 cm^2), a scaled up electrode will likely require mitigation strategies. Using data extracted from images of the evolving bubble, it is shown that there is interaction between the bubble induced convection and optical losses which causes the optical losses to plateau.

The simulation results of the resistive losses in a typical substrate used in PEC water splitting (FTO) shows there will be a significant electric potential distribution within substrate. This leads to undesirable non-uniformity in the current density distribution which demonstrates the poor scalability of such substrates. This scale-up issue could be circumvented though use of a hybrid substrate where charge is extracted from the low performance substrate by thin but highly conductive metal fingers. These results also demonstrate an interesting feature specific to photo-electrode, that if the photo-electrode is operated in the saturation region of the photo-response (*i.e.* higher potentials for a photo-anode) it can tolerate a greater potential inhomogeneity in the substrate, than if the photo-electrode is operated at the maximum power point.

A original membrane-less photo-electrochemical reactor design is proposed which separates the dissolved products *via* forced convection, whilst suppressing bubble formation. This reactor design removes the energetic losses associated with the membrane and intrinsically reduces the ohmic pathlength. Therefore, this design reduces the required photo-voltage which in turn relaxes the requirements demanded from the semiconductor(s). This design also allows for stacking multiple electrochemical cells optically in series, this would benefit materials with a low absorption length in comparison to the path length of charge carriers (*e.g.* metal oxides). The generic operational design space was determined using non-dimensional analysis and numerical modelling, and it was found that the performance is significantly impacted by the aspect ratio (AR) and the aspect ratio divided by Péclet number (AR/Pe). A full multi-physics model, using experimental data from Fe_2O_3 as a case study, was developed to verify the assumptions made and assess the efficiency increase with multiple PEC cell stacked.

Experimental results of the membrane-less PEC reactor are promising but a better method of measuring the dissolved hydrogen concentration is required. Separation efficiencies of up to *ca.* 90% are demonstrated, which would need to be improved

but does demonstrate product separation through forced convection and acts as first benchmark on which to improve upon.

9.2 Future work proposal

There are many avenues for future work due to the complexity involved in scaling up PEC reactors. In particular, the following suggested future work would build upon this thesis.

Firstly, the open source limiting efficiency model could be extended to include realistic energetic losses [64, 65, 67, 68] so as to model practical devices. Along with a more user-friendly interface, it could be a very useful tool for a wider audience than just those interested in the fundamental limits of water splitting.

The etaPEC script could be used to compare limiting efficiency of designs within a larger systematic review of experimental demonstration in order to uncover trends in the field. From this, the underlying reason for performance improvements could be examined.

In Chapter 5, a theoretical model of the optics of bubbles was only briefly investigated, and relied on more of an empirical model rather than a model derived from a fundamental understanding of the phenomena. Therefore, ray tracing optics could be used [168] and coupled with a hydrodynamic simulation of bubble evolution, and this extended model could take into account the other negative impacts of bubbles (*e.g.* electrode blocking, effective conductivity decrease *etc.*). This would allow the assessment of which losses dominate and give fundamental insights into the complex and understudied interaction of bubbles on PEC device performance.

As stated in Chapter 8, more experimental verification of the membrane-less PEC reactor is needed to demonstrate a suitable collection efficiency. Once this is achieved, an experimental assessment of the stacked design (multiple PEC cell) could be undertaken, with the film thickness of the semiconducting material optimised for a certain number of stacked PEC cell. This could improve the efficiency of traditionally low performing materials such as metal oxides. Light illumination from both sides, pressurisation and solar concentration could also be investigated.

Finally, a greater number of experimental demonstrations of scalable PEC reactors still need to be built. A necessary step to realise the potential of photo-electrochemical water splitting to capture and store the solar energy, is the engineering of devices and systems. As both PEC material and reactor development will be mutually dependent, the challenges of each cannot be considered in isolation but tackled concurrently.

Chapter 10

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Chapter 11

Appendices

11.1 Appendix A: Non-linear circuit analysis

The non-linear circuit analysis (tableau matrix analysis) [91] used in the efficiency modelling (Chapter 3) is outlined here.

Tableau matrix analysis:

Notation:

A_{PV}	Illuminated area	n	Total number of nodes
b	Total number of branches	v_j	Voltage at branch j
j_j	Current at branch j	ϕ_i	Electric potential at node i
J_{PV}	Current density of PV		

1. Construct the directed graph of the circuit where the electrolyser(s) connects the first (1) and last node (n) and is final branch (b). Then, the negative side of the electrolyser(s) becomes the datum node and therefore $\phi = 0$ here.
2. Formulate a reduced-incidence matrix, I by removing the row associated with the datum node
3. Apply Kirchoff's current law to each node (except the datum node)

$$I \cdot j = 0 \quad [n-1 \text{ equations}]$$

4. Apply Kirchoff's current law to each node

$$v - I^T \cdot \phi = 0 \quad [b \text{ equations}]$$

5. Construct the branch equations:

- PV equations (for $j = 1$ to $b - 1$):

$$\begin{cases} j_j - J_{PV}(v_j)A_{PV} = 0 & \text{if PV branch} \\ v_j = 0 & \text{if electrical connection branch} \end{cases} \quad [\text{b-1 equations}]$$

- Electrolyser equation (for $j = b$)

$$v_j - V_{total} = 0 \quad [1 \text{ equations}]$$

6. The resulting set of $2b + n - 1$ equations (KCL, KVL, branch eq.) can be expressed as the following equation and solved using non-linear numerical methods.

$$F(\mathbf{i}, \mathbf{v}, \boldsymbol{\phi}) = 0$$

In order to solve the system of equations, non-linear root finding methods were implemented in MATLAB *via* the inbuilt function: `fsolve`. Additionally, each dimensional quantity was scaled prior to numerical solution in order to aid the algorithm. The scaling factors for Amperes was $j^* = \max(J_L)$ and for Volts was $v^* = e^* = V_{electrolysis}$.

As the numerical method is iterative, it requires an initial guess the variables to be solved for: $\mathbf{i}, \mathbf{v}, \boldsymbol{\phi}$. Heuristics for a good initial guess was found through trial and error, in order to prioritise finding the solution over the speed of convergence. The initial guess was calculated from the configuration and input parameters, rather than supplied by the user, so as to simplify the solution process and ensure the greatest chance of solution finding.

The heuristic for the initial guesses of branch currents $\mathbf{j}$ and voltages $\mathbf{v}$ are given in Eq. (11.1), and depend on whether the branch in question is representing a photo-absorber, a simple electrical connection, or an electrolyser or electrolyses in series. The photo-absorber current at maximum power point is denoted by j^{mpp} .

$$v_{ij} = \begin{cases} v^{mpp} \\ 0 \\ V_{electrolyser} \end{cases} \quad j_{ij} = \begin{cases} j^{mpp} & \text{branch = PV} \\ 0 & \text{branch = electrical connection} \\ \max(j^{mpp}) & \text{branch = electrolyser} \end{cases} \quad (11.1)$$

For the electric potential at each node $\boldsymbol{\phi}_0$, an initial guess was constructed from Kirchhoff's Voltage Law (*cf.* Step 4 of Tableau matrix analysis) by finding the value of $\boldsymbol{\phi}$

that minimises the residual (*cf.* Eq. (11.2)). This is then calculated with a non-linear least-squares algorithm using the inbuilt MATLAB function: `lsqnonlin`.

$$\min_{\phi_0 \in \mathbb{R}} \left(\sum_{\forall i} r_i^2 \right) \quad \text{where} \quad \mathbf{r} = \mathbf{v} - \mathbf{I}^T \phi_0 \quad (11.2)$$

11.2 Appendix B: Home-made potentiostat - DStat

A home-made potentiostat was fabricated following the instructions outlined in: M. D. M. Dryden, A. R. Wheeler, “DStat: A Versatile, Open-Source Potentiostat for Electroanalysis and Integration”, *PLOS ONE* **2015**, *10*, (Ed.: D. T. Eddington), e0140349.

The Wheeler Lab DStat is licensed under an open hardware licence (CERN OHL v. 1.2) and was designed for analytical electrochemistry. It, therefore, has an impressive low current detection resolution and features a Atmel ATXMEGA256A3U microprocessor, a 16-bit DAC, a 24-bit ADC and is powered by the USB port. The inventors place the low current limit of detection at approximately 600 fA.

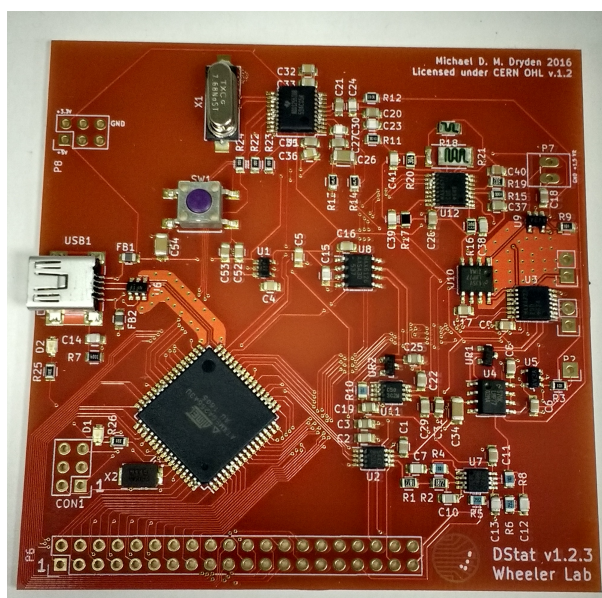


Figure 11.1: A photograph of the DStat potentiostat

11.3 Appendix C: Code repositories

From the thesis, two scripts written in MATLAB have been released under open source licences (GNU General Public License v3.0). They are as follows:

1. etaPEC - calculates the maximum theoretical solar-to-fuel efficiency of a PEC device based on it's configuration. Used in Chapter 3.

Description found at:

http://quicktech.imperialinnovations.co.uk/i/software_apps/etaPEC.html

Online repository found at:

<https://github.com/IsaacGentle/etaPEC>

2. Unidirectional_Bubble_Tracker - tracks spherical bubbles in one direction returning radius and velocity data. Used in Chapter 5.

Online repository found at:

https://github.com/IsaacGentle/Unidirectional_Bubble_Tracker

11.4 Appendix D: Membrane-less PEC reactor modelling - extra details

In this section, the discretisation of the equations used to model the membrane-less PEC reactor is outlined along with comments on the solution process.

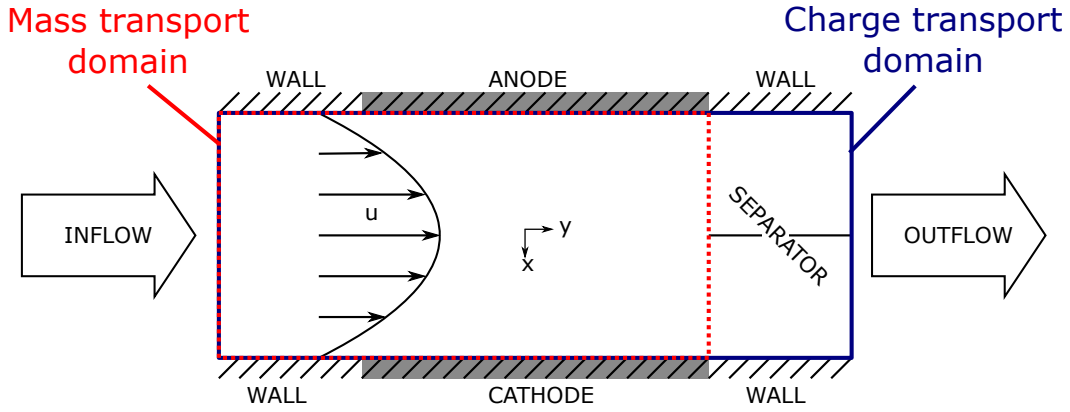


Figure 11.2: Diagram of the model domain for mass transport and charge transport within the electrolyte

11.4.1 Constant electrode flux mass transfer model

Equations

The diffusion-convection equation for species i is given in Eq. (11.3) for two dimensions, assuming steady state, and $u_x = 0$. Here, the diffusivity of species i is a positive known constant that is not spatially dependant: *i.e.* $D_i \neq f(x, y)$.

$$D_i \frac{\partial^2 c_i}{\partial x^2} + D_i \frac{\partial^2 c_i}{\partial y^2} - u_y \frac{\partial c_i}{\partial y} = 0 \quad (11.3)$$

The electrolyte velocity, $\mathbf{u} = (u_x, u_y)$, has only one non-zero component: u_y . The fluid velocity is dependant on x only by the analytic function given by equation (11.4).

$$u_y = \frac{1}{2\mu} \Delta P_{drop} (L_x x - x^2) \quad (11.4)$$

Domain

The domain for the mass transfer model can be seen in Figure 11.2 and differs from the domain of the current density distribution model. The exit channels (from the

separator onwards) are not included for simplicity which means the fluid velocity in the whole domain can be approximated by a simple analytic function given in Eq. (7.4). As convective transport is far stronger than diffusive, the choice of this more simplistic domain is valid. Furthermore, simulation of the outlets would not give useful results as the concentration distribution at this point of separation is of interest, rather than at the actual outlets of the reactor.

Boundary conditions

The boundary conditions are given in equations (11.5) - (11.9). The outlet boundary condition is only valid if the concentration of solution downstream does not affect the concentration solution upstream of the boundary. This can be assumed to be accurate as the diffusive transport counterflow will be far smaller than the convective transport out of the cell. The electrode conditions depends on whether the species i is being consumed or produced. If the species is being consumed (*via* the back-reaction), as the thermodynamic driving force is so great that it can be assumed the reaction rate is fast enough to lead to a zero concentration of reactant on the surface. The production of species i is modelled as a constant flux which is not dependent on position in the cell (*i.e.* assuming uniform current density).

$$c_i = c_{i,0} \quad \text{at inlet} \quad (11.5)$$

$$\frac{\partial c_i}{\partial y} = 0 \quad \text{at outlet} \quad (11.6)$$

$$-\vec{n} \cdot \mathbf{N}_i|_{x=0 \text{ or } L_x} = 0 \quad \text{at walls} \quad (11.7)$$

$$-\vec{n} \cdot \mathbf{N}_i|_{x=0 \text{ or } L_x} = R_{i,electrode} \quad \text{at producing electrode} \quad (11.8)$$

$$c_i = 0 \quad \text{at consuming electrode} \quad (11.9)$$

As $u_x = 0$, the boundary conditions can be written in terms of the concentration using $\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i$. Therefore, equations (11.7) - (11.8) are rewritten as neumann boundary conditions in Eq. (11.10) - (11.11). The rate of reaction can be related to the electrode current density *via* Faraday's law of electrolysis assuming a faradaic efficiency of unity.

$$\text{Anodic:} \quad \frac{\partial c_i}{\partial x} \Big|_{x=0} = \begin{cases} 0 & \text{at insulating wall} \\ -R_{i,anode}/D_i & \text{at electrode} \end{cases} \quad (11.10)$$

$$\text{Cathodic:} \quad \frac{\partial c_i}{\partial x} \Big|_{x=L_x} = \begin{cases} 0 & \text{at insulating wall} \\ R_{i,cathode}/D_i & \text{at electrode} \end{cases} \quad (11.11)$$

Discretisation

As the equations solved for concentration c_i for each species i are of the same form, for the rest of this section on the discretisation of the equations, the following discretisation notation will be used and $c = c_i$, $u = u_y$ in order to avoid confusion. The space is discretised into a finite number of points: $x_0, \dots, x_{n_x}$ and $y_0, \dots, y_{n_y}$ where $x_i = i\Delta x$ for each $i \in \{0, \dots, n_x\}$ and $y_j = j\Delta y$ for each $y \in \{0, \dots, n_y\}$. The dimensions of the channel will therefore be $L_x = n_x\Delta x$ and $L_y = n_y\Delta y$.

The mass transport equation (Eq. (11.3)), can then be discretised as given in Equations (11.12) - (11.14). Here, the notation $c_{i,j} = c(x_i, y_j)$ is used for the concentration. The 2nd order derivatives are discretised with 2nd order body centred finite difference scheme (Eq. (11.12) & (11.13)). For the 1st order derivative $\frac{\partial c}{\partial y}$, a 2nd order upwinding scheme is used as the velocity (u_y) is always strictly positive.

$$\frac{\partial^2 c}{\partial x^2} = \frac{c_{i+1,j} - 2c_{i,j} + c_{i-1,j}}{(\Delta x)^2} \quad (11.12)$$

$$\frac{\partial^2 c}{\partial y^2} = \frac{c_{i,j+1} - 2c_{i,j} + c_{i,j-1}}{(\Delta y)^2} \quad (11.13)$$

$$\frac{\partial c}{\partial y} = \frac{3c_{i,j} - 4c_{i,j-1} + c_{i,j-2}}{2\Delta y} \quad (11.14)$$

The boundary conditions are then discretised as follows:

$$c|_{x=0} = c_{0,j} \quad (11.15)$$

$$c|_{x=L_x} = c_{n_x,j} \quad (11.16)$$

$$\frac{\partial c}{\partial x}\bigg|_{x=0} = \frac{c_{2,j} - c_{0,j}}{2\Delta x} \quad (11.17)$$

$$\frac{\partial c}{\partial x}\bigg|_{x=L_x} = \frac{c_{n_x+1,j} - c_{n_x-1,j}}{2\Delta x} \quad (11.18)$$

$$c|_{y=0} = c_{i,0} \quad (11.19)$$

$$\frac{\partial c}{\partial y}\bigg|_{y=L_y} = \frac{c_{i,n_y+1} - c_{i,n_y-1}}{2\Delta x} \quad (11.20)$$

$$(11.21)$$

The resulting linear set of equations were arranged as sparse matrices and solved using an inbuilt linear solver (MATLAB).

11.4.2 Multi-physics model

11.4.3 Optics

The numerical implementation of the transfer matrix method was relatively simple as the resulting set of equations were algebraic. The solution method description given here is brief as Byrnes [256] give an extensive overview of transfer matrix model implementation.

The absorptance, transmittance and reflectance for the system were solved sequentially for each discretised wavelength λ . Firstly, the structure of the optical system was defined and for every layer ($k \in \{1, \dots, m\}$), a complex refractive index ($\tilde{n}_k$) at the specified wavelength λ and layer thickness (d_k) were assigned. Then, the 2×2 layer, interface and system matrices are calculated. From these matrices, the total transmittance, total reflectance total absorptance, and layer absorptance is computed. This is then repeated for each discretised wavelength.

Solution is numerically straightforward, except for a couple of points. Highly absorbing layers, where little light can pass through, result in the layer matrix tending towards Eq. (11.22).

$$L_k = \begin{bmatrix} \infty & 0 \\ 0 & 0 \end{bmatrix} \quad \text{as } d_k \rightarrow \infty \quad (11.22)$$

Therefore, in order for the transfer matrix method to be stable, when the entry in the first row and column of matrix L_k gets unacceptably large, it is replaced by some arbitrary large number which is large enough to keep numerical errors small, but small enough for the computer to handle (e.g. 1×10^{200}). Another issue with completely absorbing layers is that the system transfer matrix becomes ill-conditioned. Therefore, if light is to be shined from both sides, it can be difficult to obtain an accurate result. An easy work-around to this is to only solve for light in the forward direction, and to flip the stack in order to solve the reverse problem ‘forwards’. Assuming that the input light from both sides are incoherent with each other, the total optical power flow in the stack can then be calculated through summation.

11.4.4 Current density distribution

Equations

For the modelling of charge transport in the electrolyte, a secondary current density distribution model was used, which accounted for the electrode kinetics but neglects any mass transfer effects [138].

$$\nabla^2\Phi = 0 \quad \mathbf{j} = -\kappa\nabla\Phi \quad (11.23)$$

Domain

Figure 11.2 shows the domain in which the current density distribution model is solved, which includes the outlet of the reactor after the separator in comparison to the mass transfer model.

Boundary conditions

All the boundary conditions for this model are obtained from specifying the current density normal to the boundary. For all boundaries except for the electrodes, insulating boundary conditions were used where the current density is fixed at zero (Eq. (11.24)). For electrodes, this is equal to the electrode current density $j_{electrode}$ (Eq. (11.25)) which is a function of electrode potential E which is defined as $E = \Phi_{electrode} - \Phi(y) + \text{constant}$. Here, $\Phi_{electrode}$ is the absolute electric potential of the electrode and $\Phi(y)$ is the absolute electric potential of the electrolyte at the interface and is a function of position. In this membrane-less PEC reactor model, $\Phi_{electrode}$ is constant and Φ (electrolyte) is dependent on position, which interestingly is contrary to the dependence of these variables in the FTO resistive losses model. The arbitrary constant results from the reference electrode used.

$$-\vec{n} \cdot \mathbf{j} = 0 \quad \text{at insulating boundary} \quad (11.24)$$

$$-\vec{n} \cdot \mathbf{j} = j_{electrode} \quad \text{at electrode} \quad (11.25)$$

Then, these boundary conditions can be written in terms of the electric potential variable using the relation $\mathbf{j} = -\kappa\nabla\Phi$. Equation (11.24) becomes $\vec{n} \cdot \nabla\phi = 0$, and Eq. (11.25) becomes $\vec{n} \cdot \nabla\phi = j_{electrode}/\kappa$.

The dependence of electrode current density $j_{electrode}$ on electrode potential E , is given by the electrode kinetics and two differing relationships are used for photo-anode or cathode. For the cathode, a Butler-Volmer type relationship was used (Eq. (11.26)) where the electrode potential E of the interface can be related to the electrolyte electric potential Φ as previously mentioned. The constants α_a , α_c , E^{eq} and j_o are anodic and cathodic charge transfer coefficient, equilibrium electrode potential and exchange current density respectively and $f = F/RT$.

$$j_{cathode}(E) = j_o \left(e^{\alpha_a f (E - E_{eq})} - e^{-\alpha_c f (E - E_{eq})} \right) \quad (11.26)$$

For the photo-anode, the photo-current was calculated from integration of the experimentally determined IPCE as shown in Eq. (11.27). Here, $\eta_{IPCE}^{f/b}$ is the incident photon to current efficiency and $q_p^{f/b}$ is the spectral photon flux where the superscript f/b gives the direction of illumination (f for forward and b for backward). As the spectral photon flux q_p vanishes for small wavelengths of light and η_{IPCE} tends to zero for larger wavelengths of light, the improper integral can be accurately approximated by integrating over an appropriate interval $[\lambda_{start}, \lambda_{end}]$. A IPCE for a specific λ and E is calculated from interpolation (splines) of experimental data outlined in the main text.

$$j_{anode}(E) = \int_0^\infty q_e \left(\eta_{IPCE}^f(E, \lambda) q_p^f(\lambda) + \eta_{IPCE}^b(E, \lambda) q_p^b(\lambda) \right) d\lambda \quad (11.27)$$

Discretisation

Again, the same notation as was used in the space discretisation of the mass transport model, is used here. The Laplace equation is discretised with a 2nd order centred finite difference scheme given in Eq. (11.28). The derivatives in the boundary conditions equations are discretised using a body centred finite difference scheme given in Eq. (11.29) - (11.32). Fictional discretisation points are added just outside the solution domain (e.g. for x , points added at position 0 and $n_x + 1$), which are used to control the value of the derivative to meet the boundary condition equations.

$$0 = \frac{\Phi_{i+1,j} - 2\Phi_{i,j} + \Phi_{i-1,j}}{(\Delta x)^2} + \frac{\Phi_{i,j+1} - 2\Phi_{i,j} + \Phi_{i,j-1}}{(\Delta y)^2} \quad (11.28)$$

$$\left. \frac{\partial \Phi}{\partial x} \right|_{x=0} = \frac{\Phi_{2,j} - \Phi_{0,j}}{2\Delta x} \quad (11.29)$$

$$\left. \frac{\partial \Phi}{\partial x} \right|_{x=L_x} = \frac{\Phi_{n_x+1,j} - \Phi_{n_x-1,j}}{2\Delta x} \quad (11.30)$$

$$\left. \frac{\partial \Phi}{\partial y} \right|_{y=0} = \frac{\Phi_{i,2} - \Phi_{i,0}}{2\Delta y} \quad (11.31)$$

$$\left. \frac{\partial \Phi}{\partial y} \right|_{y=L_y} = \frac{\Phi_{i,n_y+1} - \Phi_{i,n_y-1}}{2\Delta y} \quad (11.32)$$

The resulting system of simultaneous equations is non-linear due to the electrode boundary conditions and is solved using an inbuilt Newton-Raphson procedure in MATLAB.

11.4.5 Mass transport

For the multi-physics mass transport model, the discretisation and solution is the same as in the constant electrode flux mass-transfer model with one exception: Now $R_{i,\text{left/right}}$ is a function of y which is calculated from the solution of the secondary current density model ($j_{\text{electrode}}$) using Faraday's law of electrolysis given in Eq. (11.33).

$$R_{i,\text{left/right}} = \frac{\eta_{\text{faradiac}} j_{\text{left/right}}}{n_e F} \quad (11.33)$$

11.4.6 Value of discretisation parameters

The details of the discretisation of the dimensions x , y and λ are given in Table 11.1, along with details about the geometry (*i.e.* the length of any entrance or exit). Table 11.1 also includes the details of the light discretisation in optical model: the interval $[\lambda_{\text{start}}, \lambda_{\text{end}}]$ and interval spacing $\Delta\lambda$. For the current density model, the wavelength parameters refer to the discretisation of the IPCE integration (Eq. (11.27)).

Table 11.1: Numerical solution details (where N.D.A. is Non-Dimensional Analysis)

	Model	Symbol	Value/Dataset/Notes
N.D.A.	Mass transfer	n_x	401
		n_y	401
		$L_{y,\text{entrance}}$	$= 0.5 \times L_x$
		L_y^{tot}	$= L_{y,\text{entrance}} + L_{y,\text{electrode}}$
Full multi-physics model	Optics	λ_{start}	310 nm
		λ_{end}	1000 nm
		$\Delta\lambda$	1 nm
	Current density model	λ_{start}	310 nm
		λ_{end}	600 nm
		$\Delta\lambda$	1 nm
		$L_{y,\text{entrance}}/L_y^{\text{tot}}$	0.2
		$L_{y,\text{exit}}/L_y^{\text{tot}}$	0.3
		n_x	148
		n_y	148
	Mass transfer	n_x	101
		n_y	101
		$L_{y,\text{entrance}}$	$= 0.5 \times L_x$
		L_y^{tot}	$= L_{y,\text{entrance}} + L_{y,\text{electrode}}$

11.5 Appendix E: Calculation method of effective interfaces

A test optical cell was made in order to measure the optics of the glass/thin film/electrolyte interface. A diagram of this test cell can be seen in Figure 11.3 by stacking a microscope coverslip (soda lime glass), 1 mm silicone gasket round the edge and the sample. In between the coverslip and the sample a drop of water was placed in order to mimic the optical behaviour of 1 M NaOH(aq). Then, the forward and backwards transmittance and reflectance was measured using an UV-vis spectrophotometer with an integrating sphere attachment.

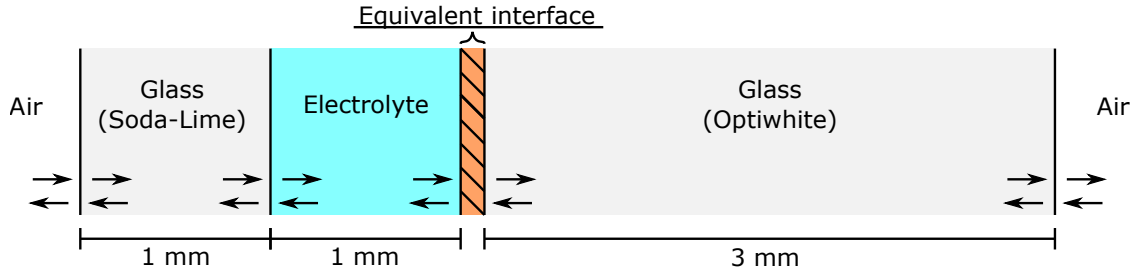


Figure 11.3: Optical geometry of the test cell for determining the equivalent interface

From the measured total transmittance and total reflectance for light from both directions, the system intensity transfer matrix $\bar{S}$ could be calculated with Eq. (11.34). The intensity reflection $\bar{r}^{+/-}$ and transmission $\bar{t}^{+/-}$ coefficients can be related to the total reflectance $R^{+/-}$ and transmittance $T^{+/-}$ by Eq. (11.35) where the superscript denotes the forward (+) and backward (-) propagating electromagnetic waves.

$$\bar{S} = \frac{1}{\bar{t}^+} \begin{bmatrix} 1 & -\bar{r}^- \\ \bar{r}^+ & \bar{t}^+ \bar{t}^- - \bar{r}^+ \bar{r}^- \end{bmatrix} \quad (11.34)$$

$$R^+ = \bar{r}^+ \quad T^+ = \bar{t}^+ \frac{\text{Real}\{\bar{n}_{j+1}\}}{\bar{n}_j} \quad R^- = \bar{r}^- \quad T^- = \bar{t}^- \frac{\text{Real}\{\bar{n}_j\}}{\bar{n}_{j+1}} \quad (11.35)$$

The system matrix can be decomposed into the constituent interface matrices and layer matrices (Eq. (11.36)) and for all the known layers (coverslip glass, electrolyte, optiwhite glass), the layer and interface matrices can be calculated. This leaves one unknown matrix, *i.e.* the equivalent interface, which can be solved for using the matrix algebra given in Eq. (11.37).

$$\bar{S} = \bar{I}_{0,1} \bar{L}_1 \bar{I}_{1,2} \cdots \bar{L}_j \bar{I}_{j,j+1}^{equiv} \bar{L}_{j+1} \cdots \bar{L}_m \bar{I}_{m,m+1} \quad (11.36)$$

$$\bar{\mathbf{I}}_{j,j+1}^{equiv} = \left(\bar{\mathbf{I}}_{0,1} \bar{\mathbf{L}}_1 \bar{\mathbf{I}}_{1,2} \cdots \bar{\mathbf{L}}_j \right)^{-1} \bar{\mathbf{S}} \left(\bar{\mathbf{L}}_{j+1} \cdots \bar{\mathbf{L}}_m \bar{\mathbf{I}}_{m,m+1} \right)^{-1} \quad (11.37)$$

The reflection and transmission coefficients for the equivalent interface can then be calculated with Eq. (11.38).

$$\bar{r}^+ = \frac{\bar{S}_{21}}{\bar{S}_{11}} \quad \bar{t}^+ = \frac{1}{\bar{S}_{11}} \quad \bar{r}^- = -\frac{\bar{S}_{12}}{\bar{S}_{11}} \quad \bar{t}^- = \frac{\det(\bar{\mathbf{S}})}{\bar{S}_{11}} \quad (11.38)$$

In order to test the accuracy of the optical data (soda lime glass [269]) with the glass coverslip, only the transmittance and reflectance of the coverslip only was measured and modelled. The results can be seen in Figure 11.4 and show close similarity between measured and predicted. Therefore, the assumption that the glass coverslip was made of soda lime glass is validated.

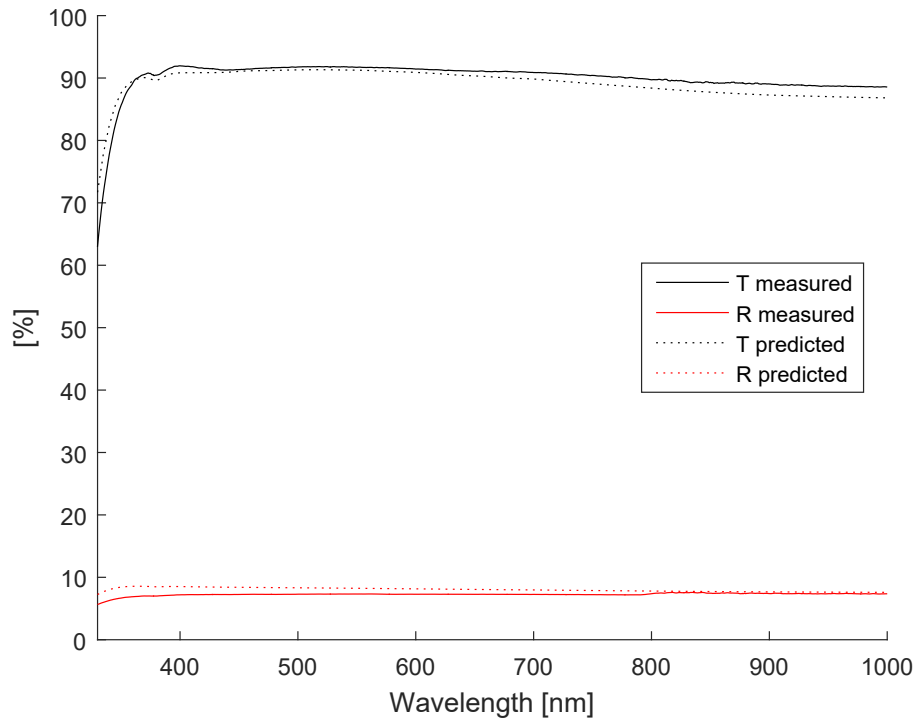


Figure 11.4: Measured and simulated transmittance and reflectance of the glass coverslip, assuming soda lime glass complex refractive index data [269]

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I hope this answers your questions. Let me know if I can provide any more detail.

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