Imperial College London

Photo-Electrochemical Production of H_2 Using Solar Energy

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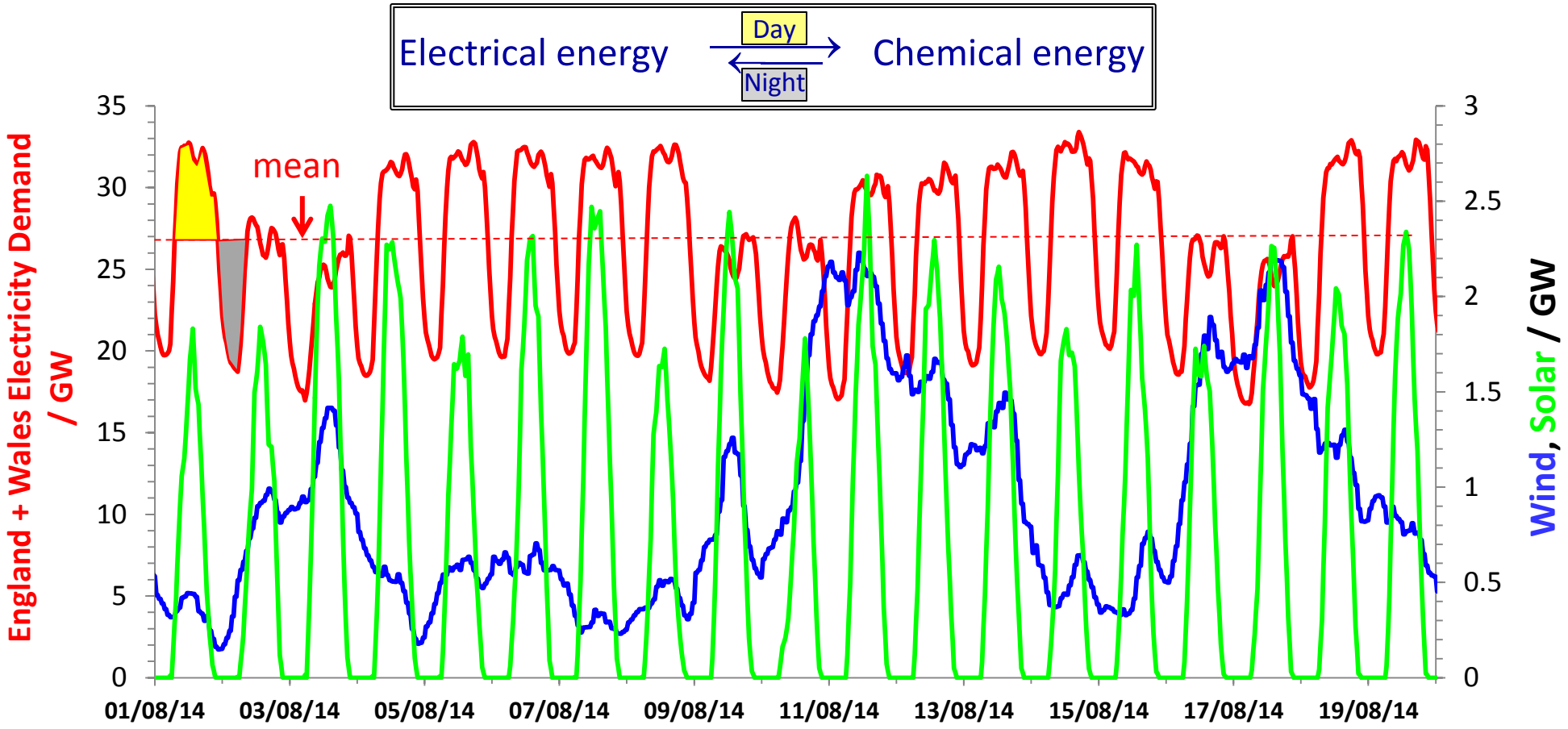
- Motivation for solar energy harvesting with storage of H_2
- Problems of photo-electrochemical reactor designs
- Modelling of potential and current density distributions for reactor design

Time Dependence of Electrical Power Demand + Renewable Supply in UK



UK has only 27.6 GW h of pumped-hydro energy storage; fluctuations in electrical power demand and supply require more, especially with decreasing spare power generation capacity

Source: www.nationalgrid.com/uk

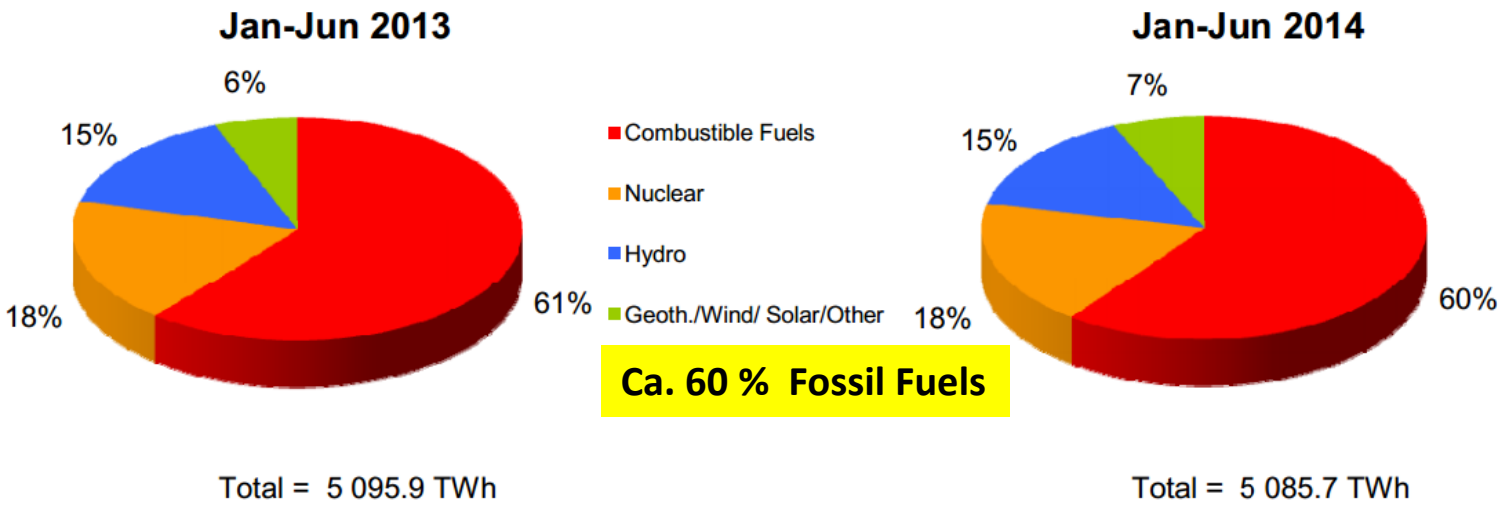
Technological Objectives

- Smooth dynamics of electrical power demands
- Manage intermittency of renewable power sources

→ **Storage of electrons reversibly in chemical bonds at grid scale**

Chemical bonds → High specific energies

- Decarbonise power sources, especially for electric and hybrid vehicles



OECD Electricity Production (IEA)

ASTM G173-03 Reference Solar Spectrum: Terrestrial Direct Normal + Circumsolar

(Power density of (air mass) AM1.5 light; ca. 1 kW m^{-2} ≡ 1 Sun)

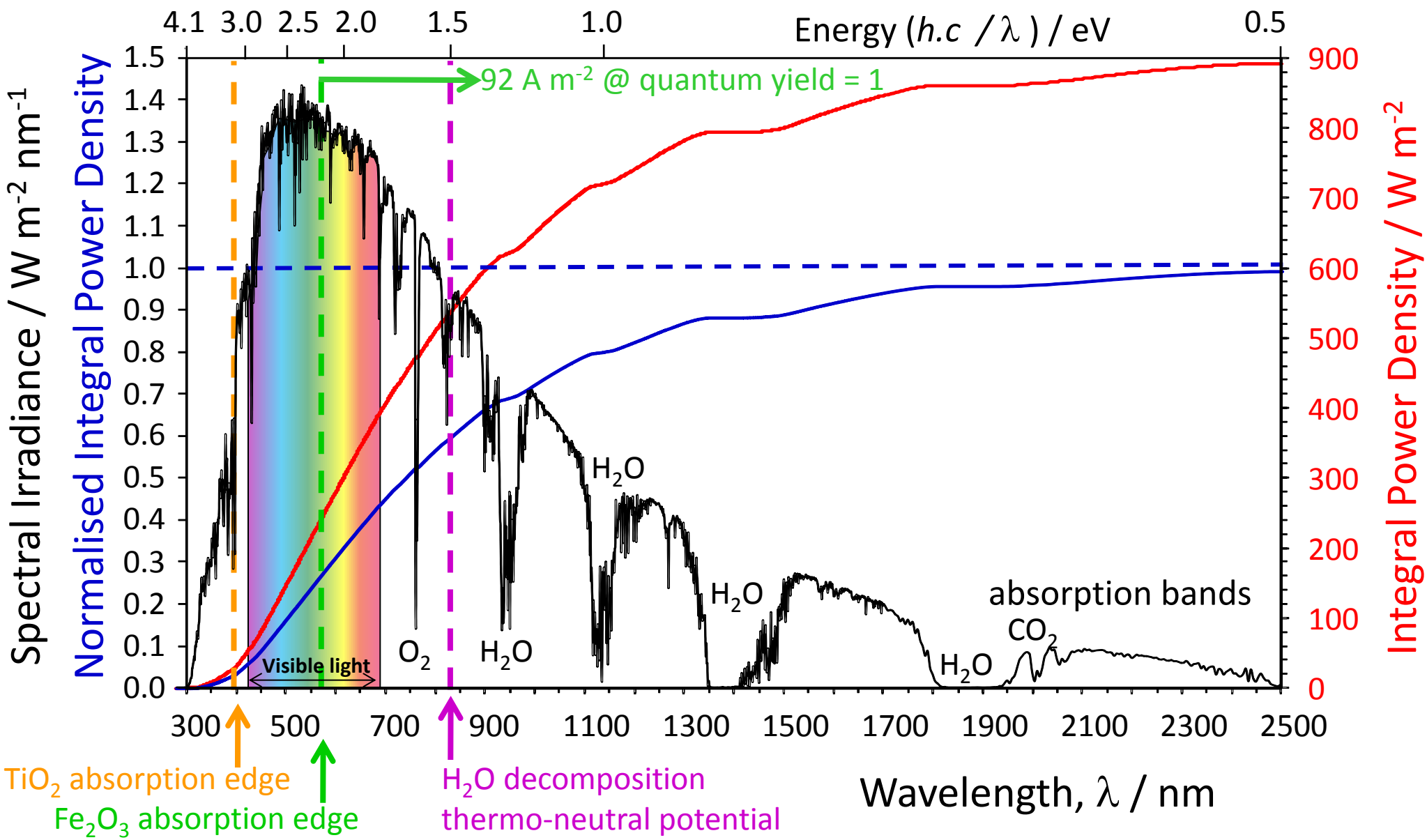


Photo-Electrochemical Reactors: Material Requirements

Absorption of *hv*:

- ✓ Absorption spectrum well matched to solar spectrum

Energy levels:

- ✓ Conduction band energy below decomposition potential for H_2O to H_2
- ✓ Valence band energy below decomposition potential for H_2O to O_2

Stability in electrolyte:

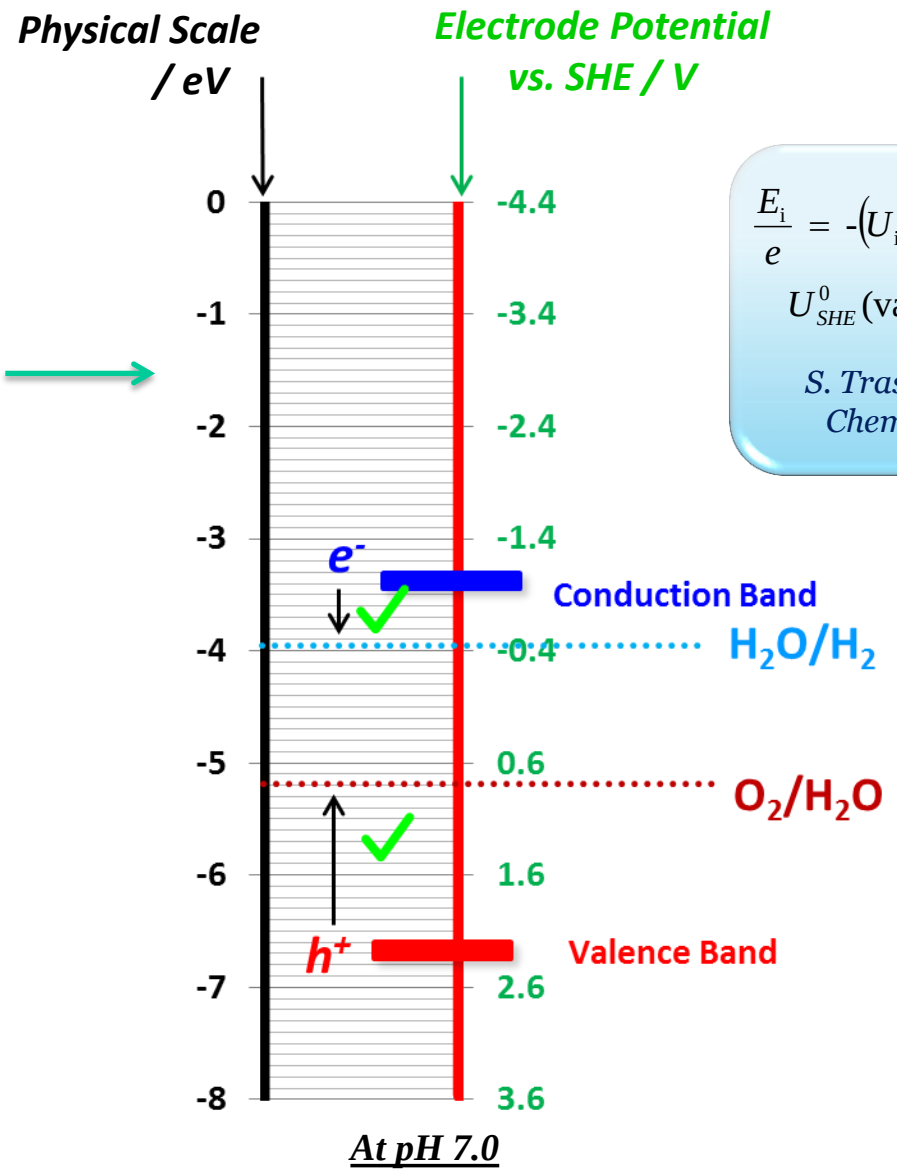
- ✓ Stable to decomposition by e^- and h^+ over wide potential & pH range

Catalysis:

- ✓ Catalysis of H_2 and O_2 evolution reactions, to minimise the rate of electron-hole recombination

Fabrication:

- ✓ Easily fabricated on large scale at low cost



$$\frac{E_i}{e} = -\left(U_i(\mathrm{SHE}) + U^0_{SHE}(\mathrm{vac})\right)$$

$$U^0_{SHE}(\mathrm{vac}) = +4.44\ V$$

*S. Trasatti, Pure & Appl. Chem., **58** (1986) 955*

Potential-pH diagram of Fe-H_2O System at 298 K; dissolved activity = 10^{-4}

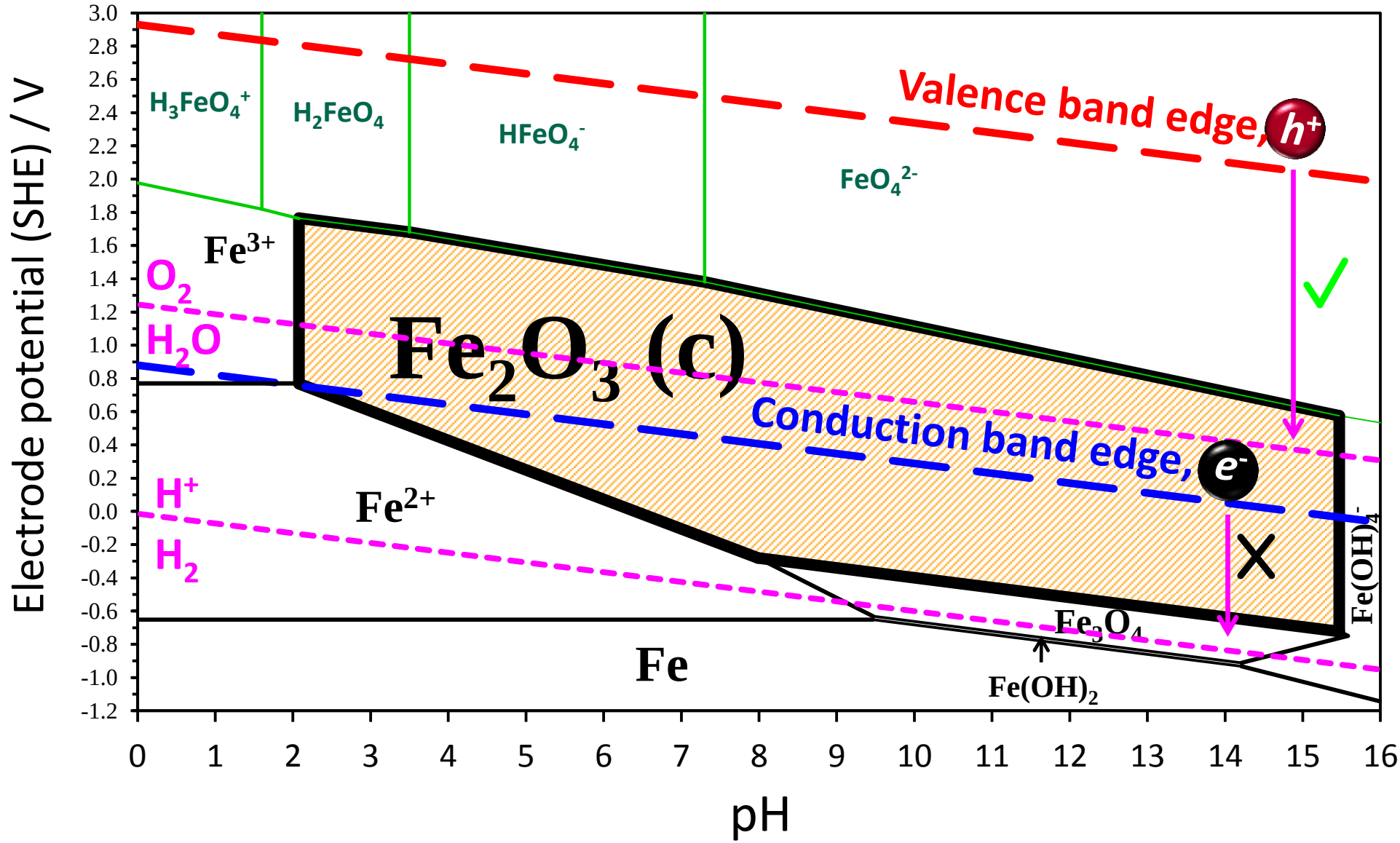
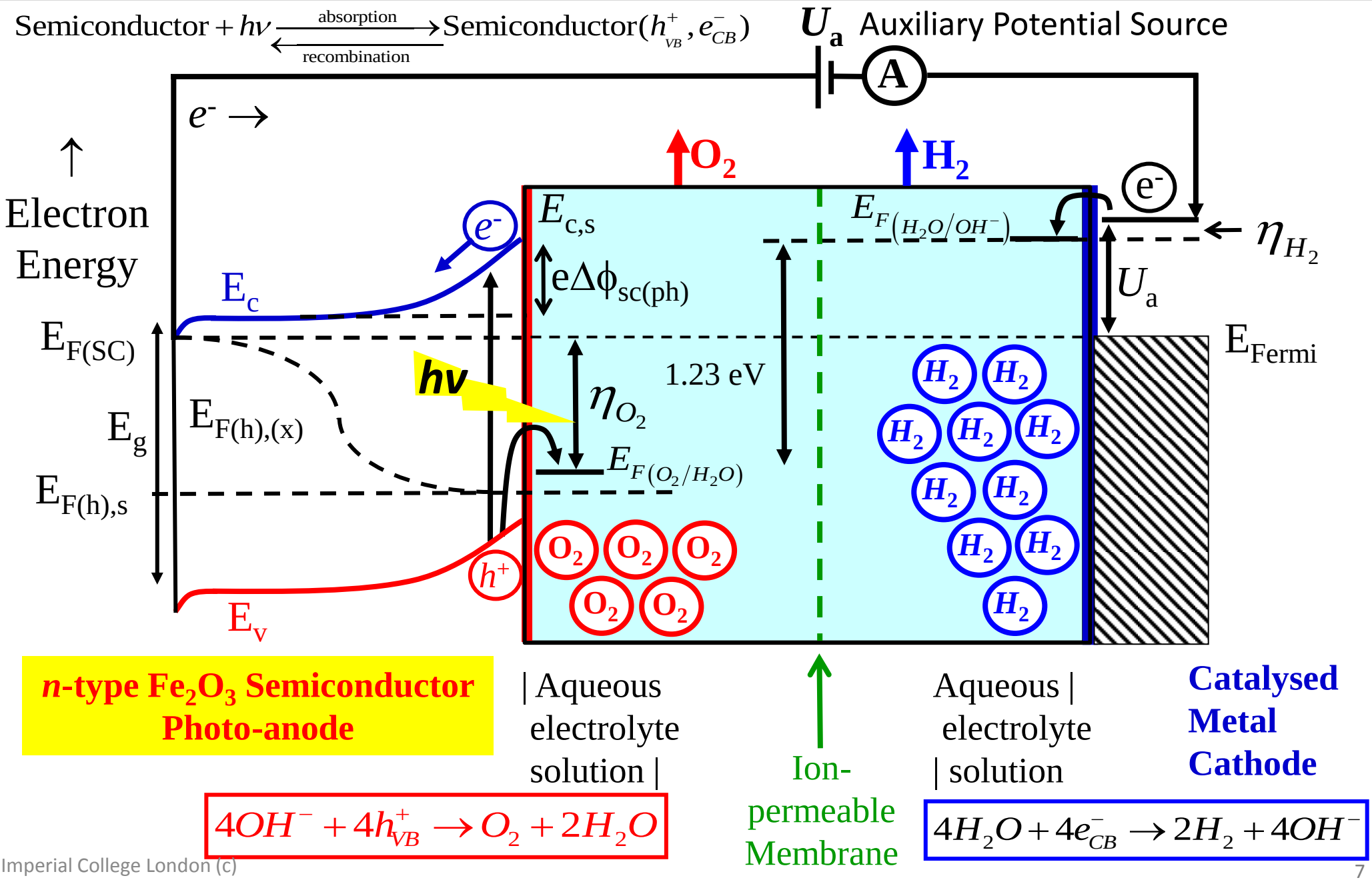
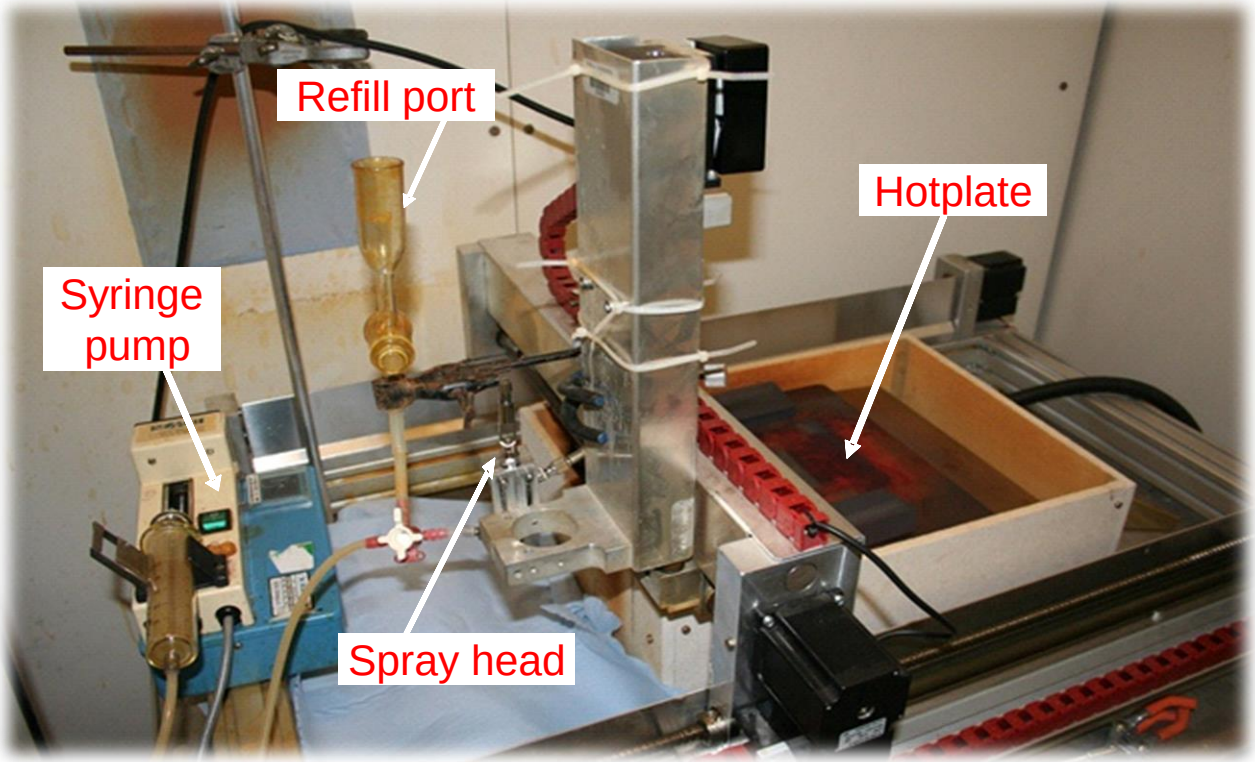


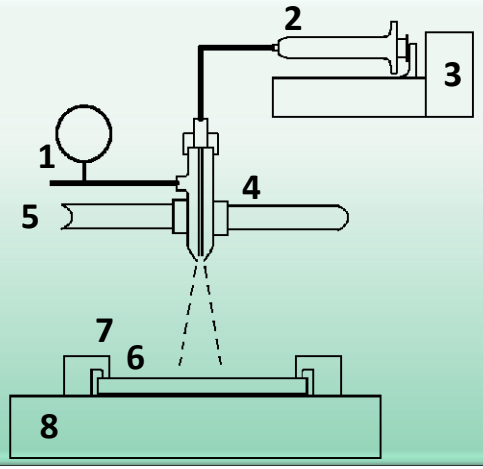
Photo-Electrochemical Reactors: Photo-assisted Electrolysis



Hematite Photo-anode Fabrication by Spray Pyrolysis on FTO or Ti Substrates

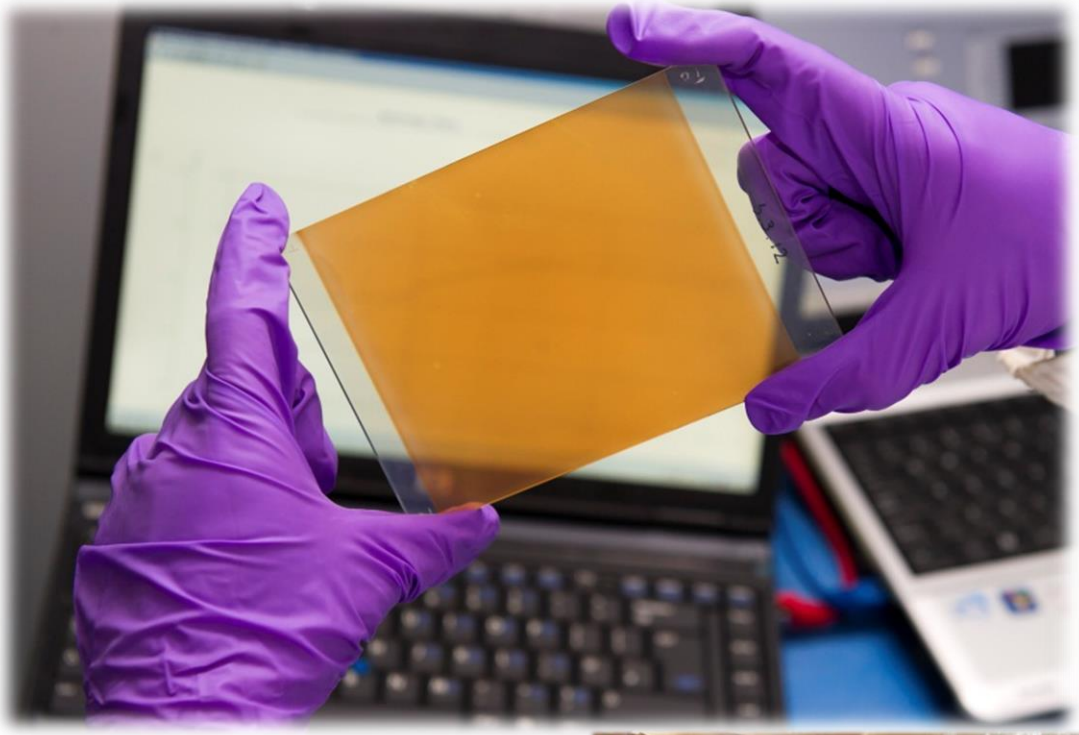


1. Compressed Air
2. Precursor reservoir
3. Syringe pump
4. Quartz nebuliser
5. CNC machine
6. Substrate
7. Clamping block
8. Hotplate



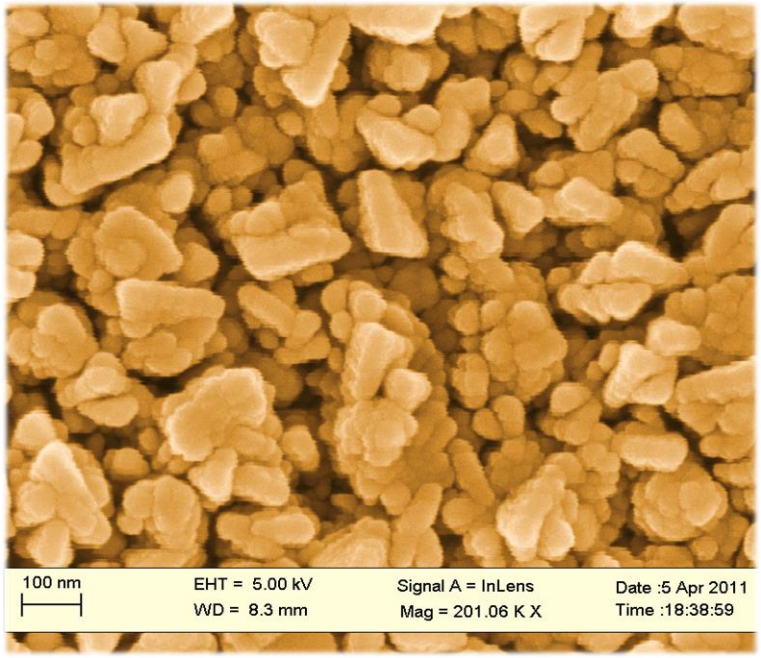
Films produced by nebulising ethanolic solutions of metal salts onto heated substrate

200 nm thick Sn^{IV}-doped Fe_2O_3 Photo-Anode Spray Pyrolysed onto Fluorine-Doped Tin Oxide Coated Glass



Potential / current distribution problems with transparent substrates (ITO, FTO etc.)

C. Carver, Z. Ulissi, C.K. Ong, S. Dennison, G.H. Kelsall, and K. Hellgardt, (2011). Modelling and development of photoelectrochemical reactor for H2 production. Int.J.Hydrogen Energy, 37(3), 2012, 2911–2923.



SEM image

Effect of Potential and (49 W m^{-2} Xe) White Light Illumination on Glass | F-doped SnO_2 | 400 nm Spray Pyrolysed Sn^{IV}-doped Fe_2O_3 | 1 M NaOH

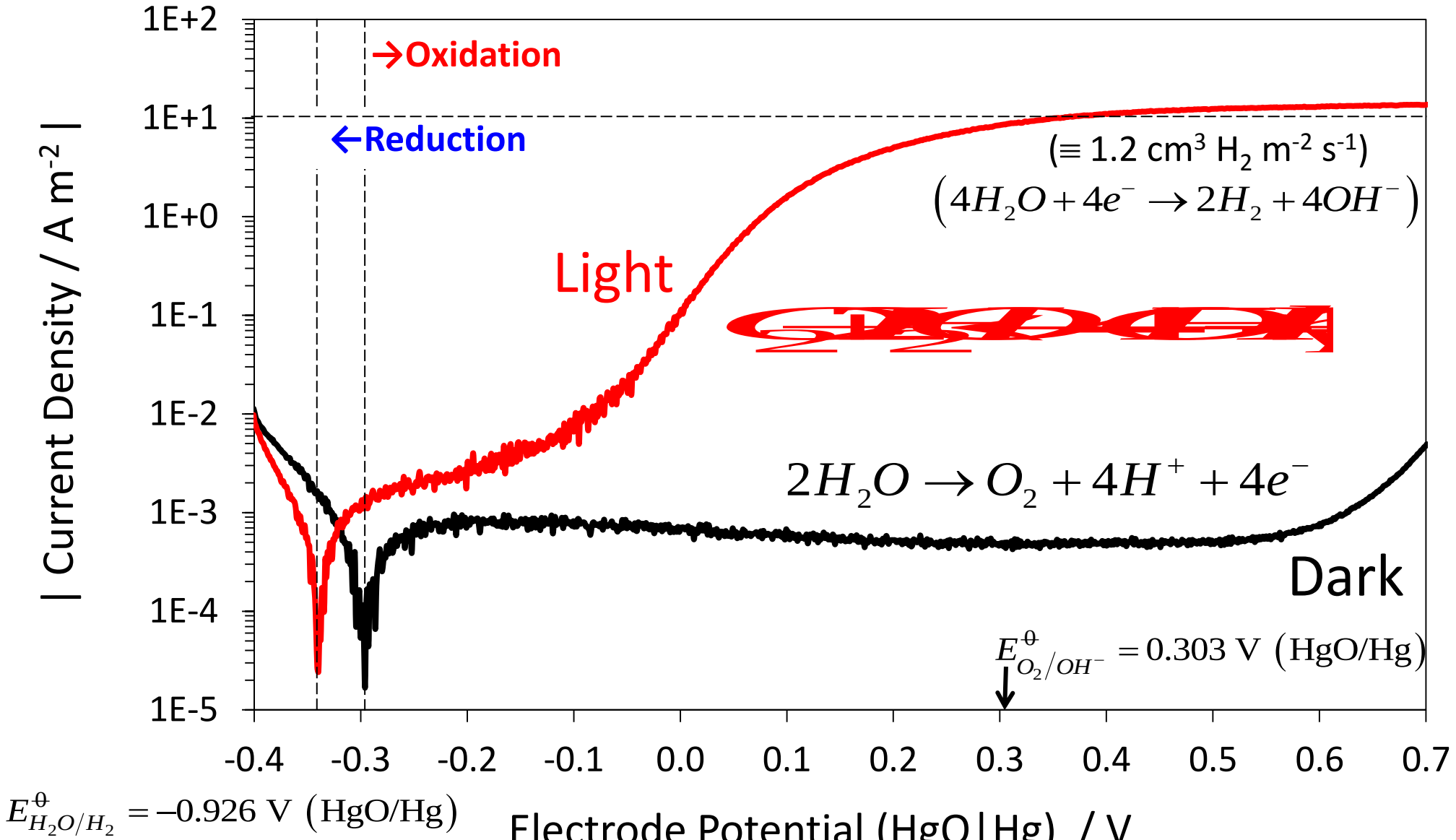


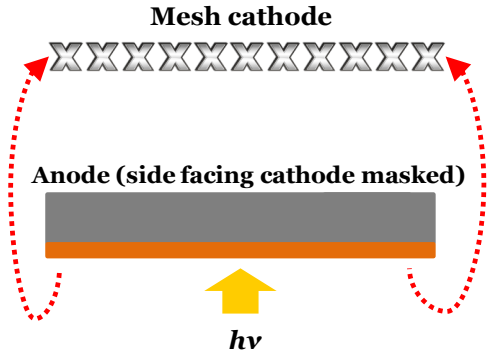
Photo-Electrochemical Reactor Design: Scale-up Options

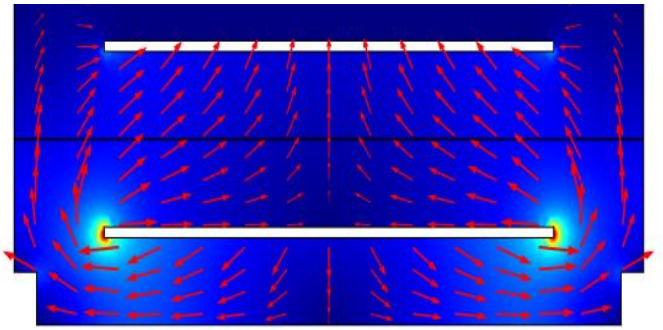
Symmetrical Vertical - Lateral Scale-up

Fe_2O_3 film facing away from cathode

✓ Even illumination

× Non-uniform current distribution

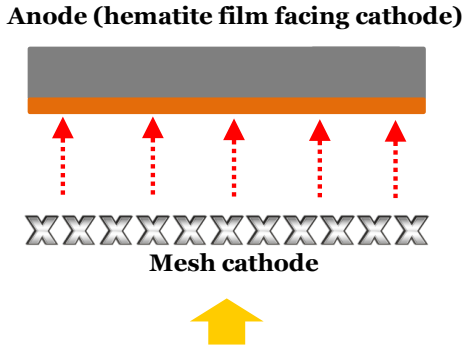


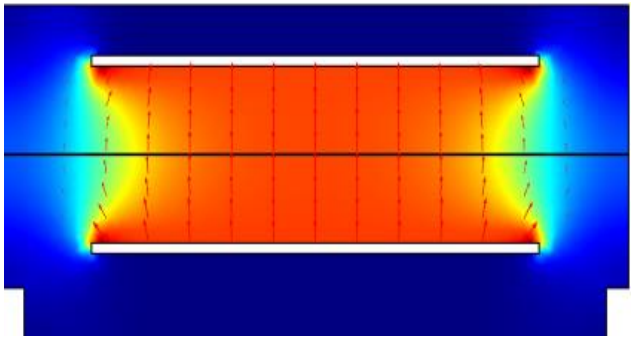


Fe_2O_3 film facing towards cathode

✓ More uniform current distribution

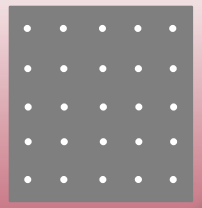
× ½ Fe_2O_3 film area in dark

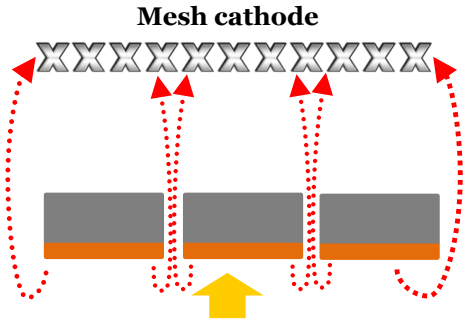




Possible Compromise

Mini cavities in photo-anode to improve current distribution





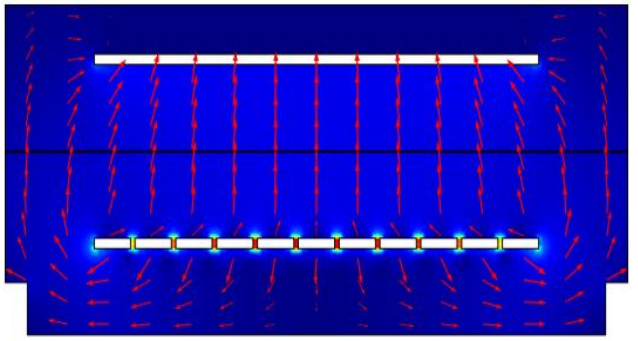
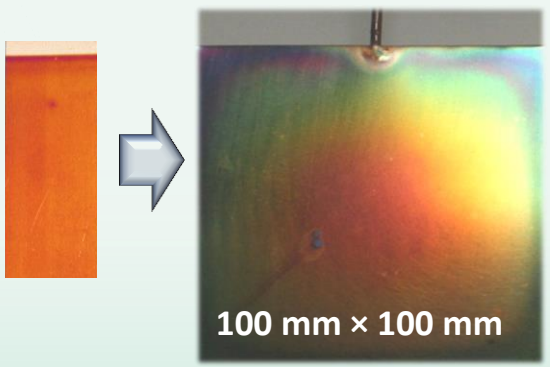
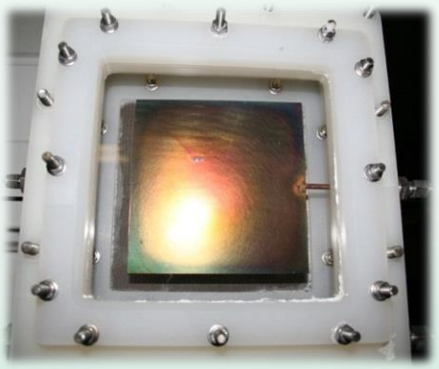
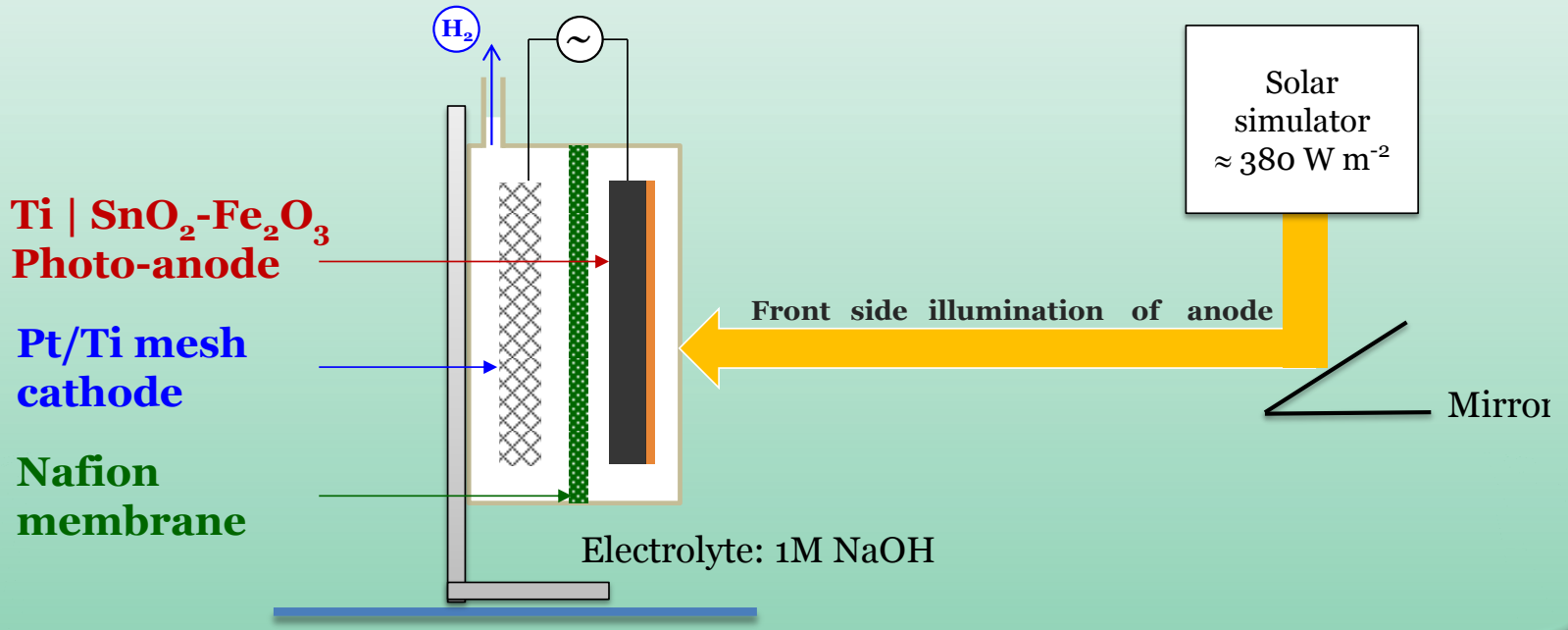


Photo-Electrochemical Reactor Design: Scale-up Options

Symmetrical Vertical - Lateral Scale-up

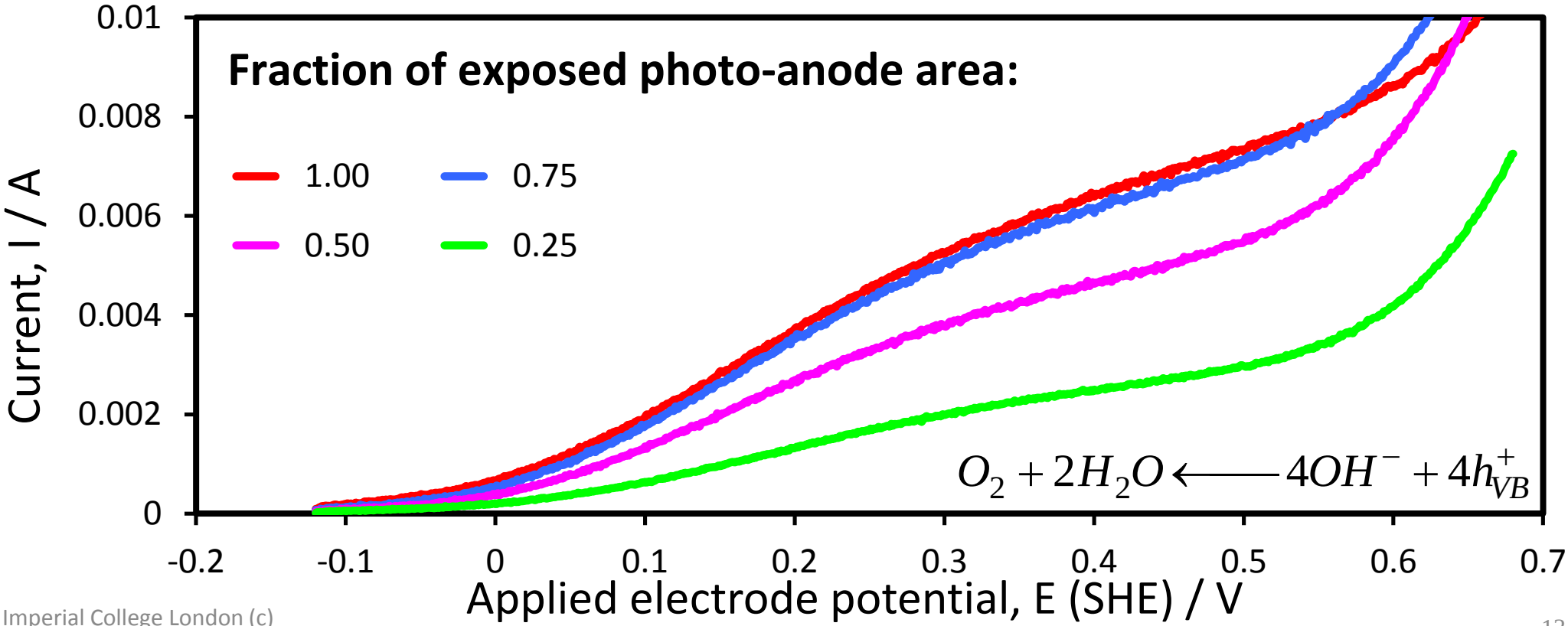




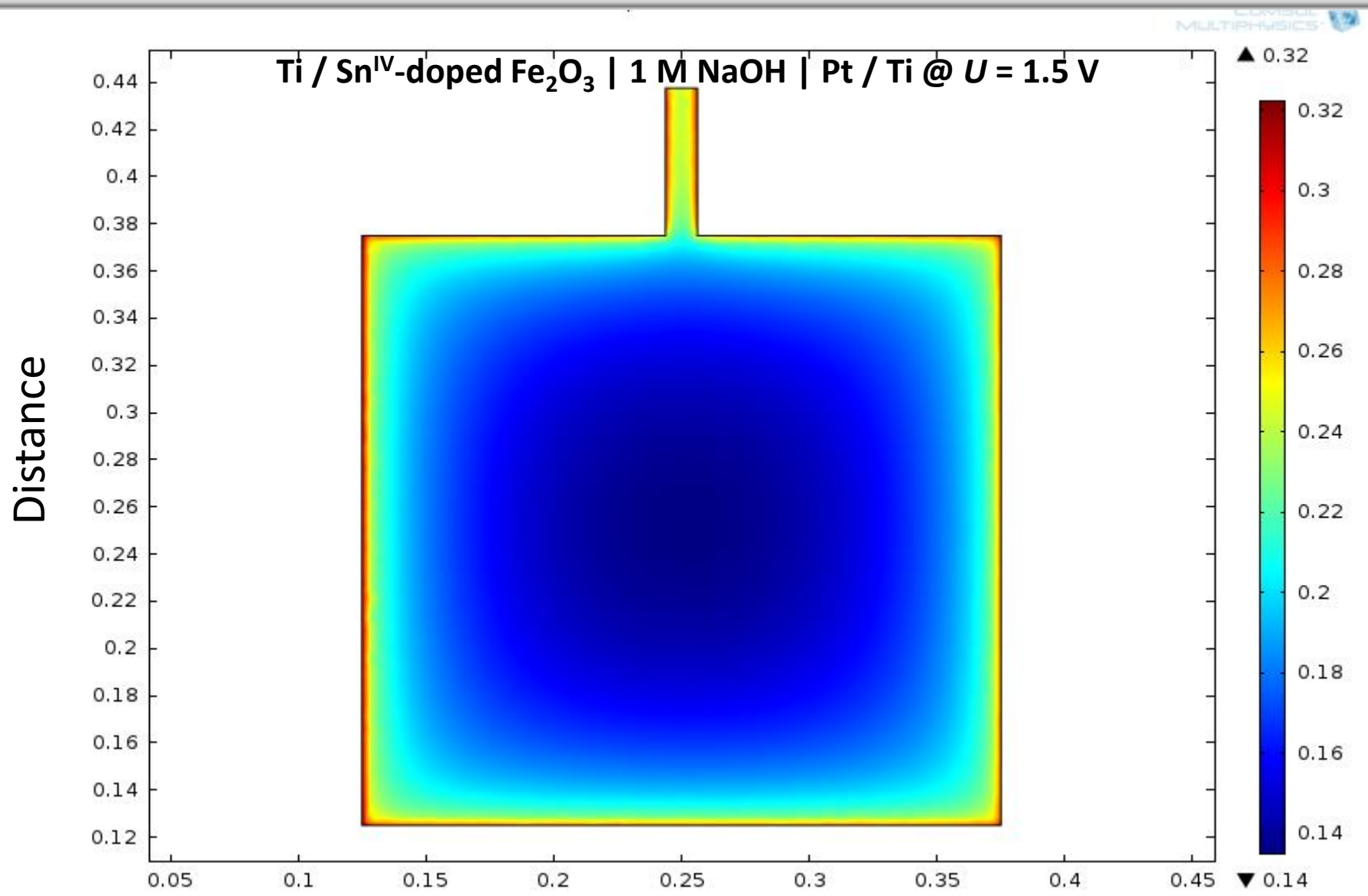


Ong C.K., Dennison S., Fearn S., Hellgardt K., Kelsall G.H., Electrochim. Acta 2014, 125, 266-274

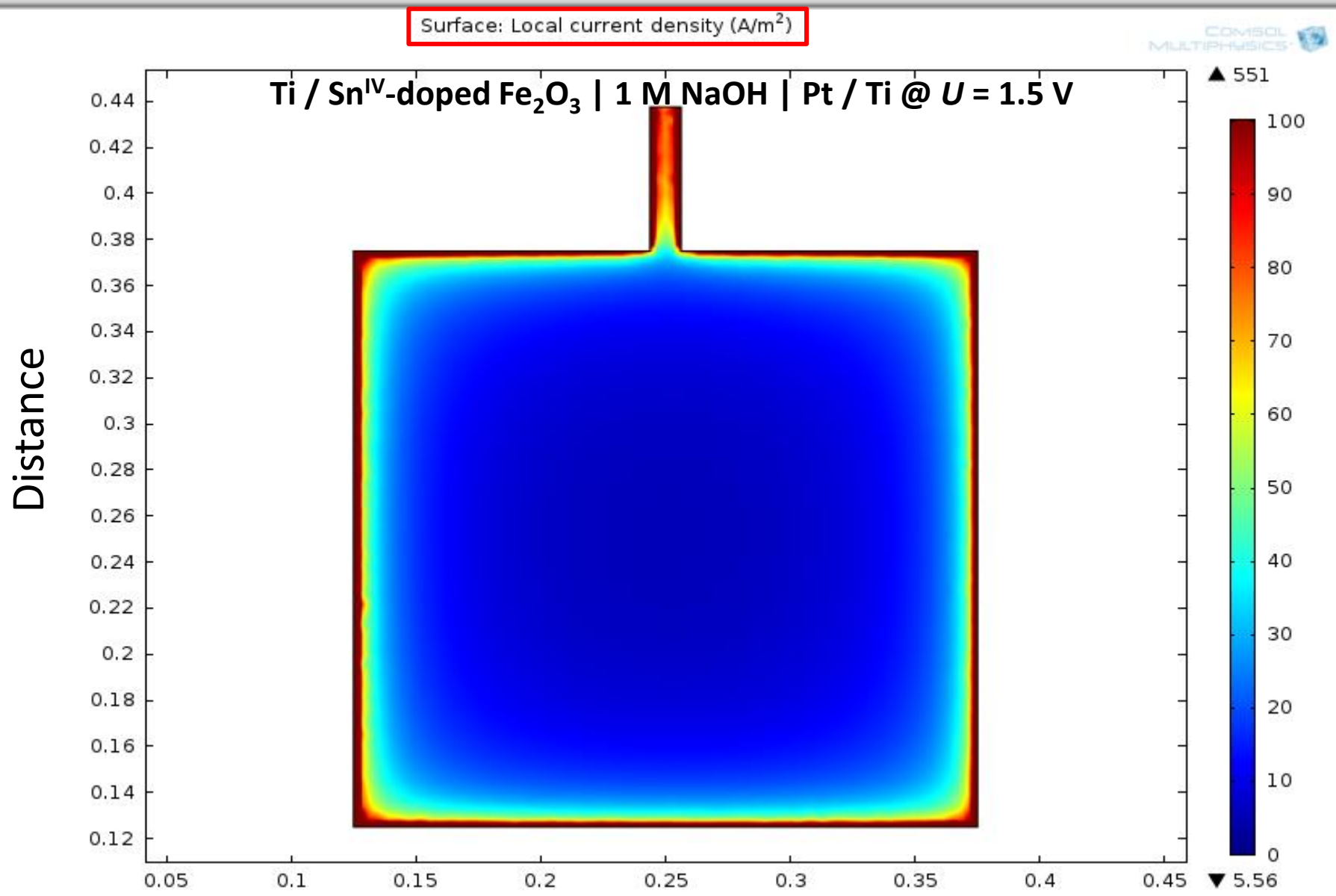
Effect of anode potential on O_2 evolution current at 0.1 × 0.1 m^2 Ti |Sn^{IV}-Fe_2O_3 anode in 1 M NaOH solution (pH ca. 13.7) with parts of surface area masked; 50 mV s^{-1}



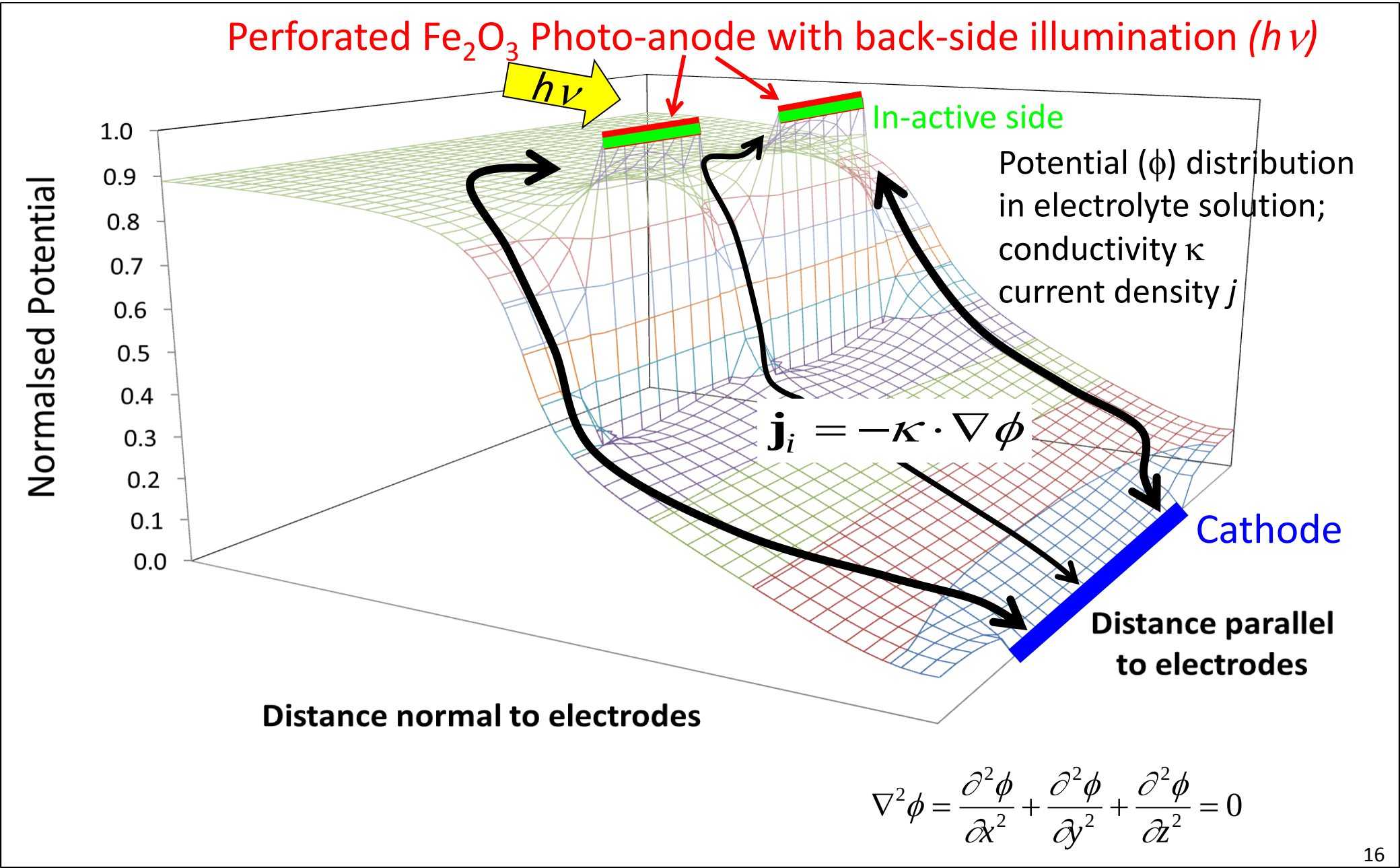
Predicted Spatial Distribution of O_2 Overpotential at 0.1×0.1 m^2 Ti |Sn^{IV}-Fe_2O_3 (Back-side) Anode in 1 M NaOH solution (pH ca. 13.7); Ti | Pt cathode



Predicted Spatial Distribution of O_2 Current Density at 0.1×0.1 m^2 Ti |Sn^{IV}-Fe_2O_3 (Back-side) Anode in 1 M NaOH solution (pH ca. 13.7); Ti | Pt cathode

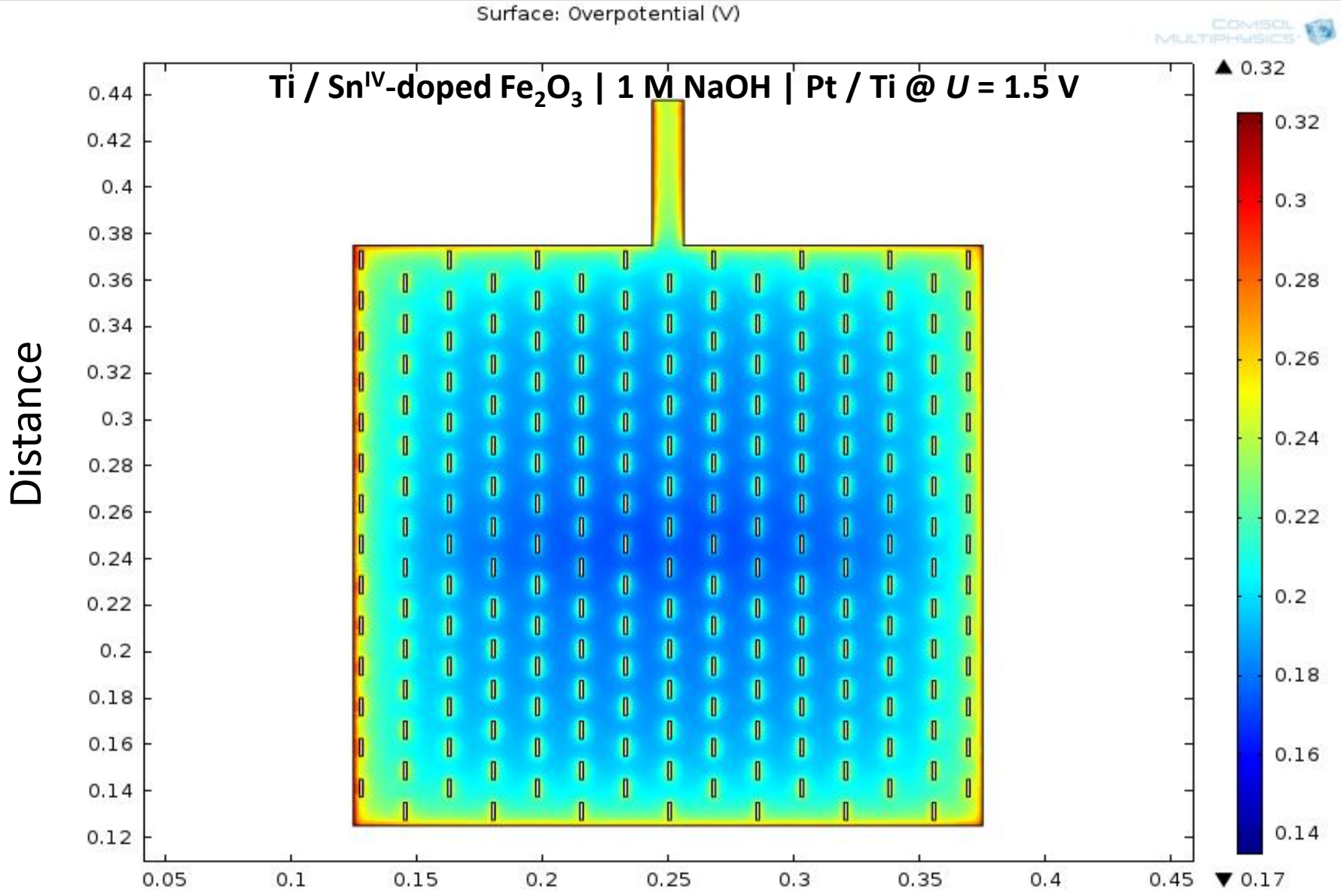


(Normalised) Primary Potential Distribution in Photo-assisted Electrolyser

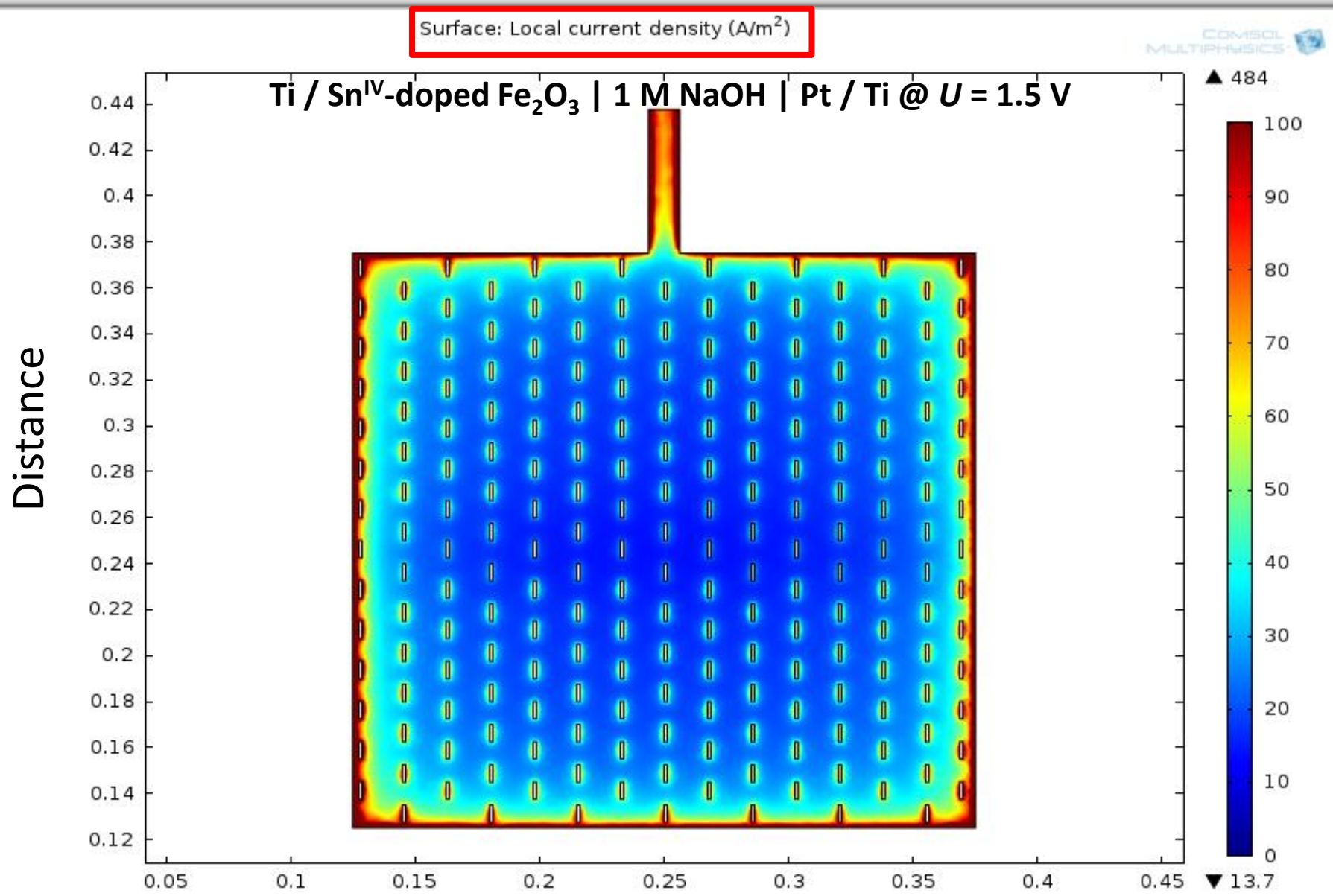


$$\nabla^2\phi = \frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} = 0$$

Predicted Spatial Distribution of O_2 Overpotential at 0.1×0.1 m^2 Ti |Sn^{IV}-Fe_2O_3 (Back-side) Anode in 1 M NaOH solution (pH ca. 13.7); Ti | Pt cathode



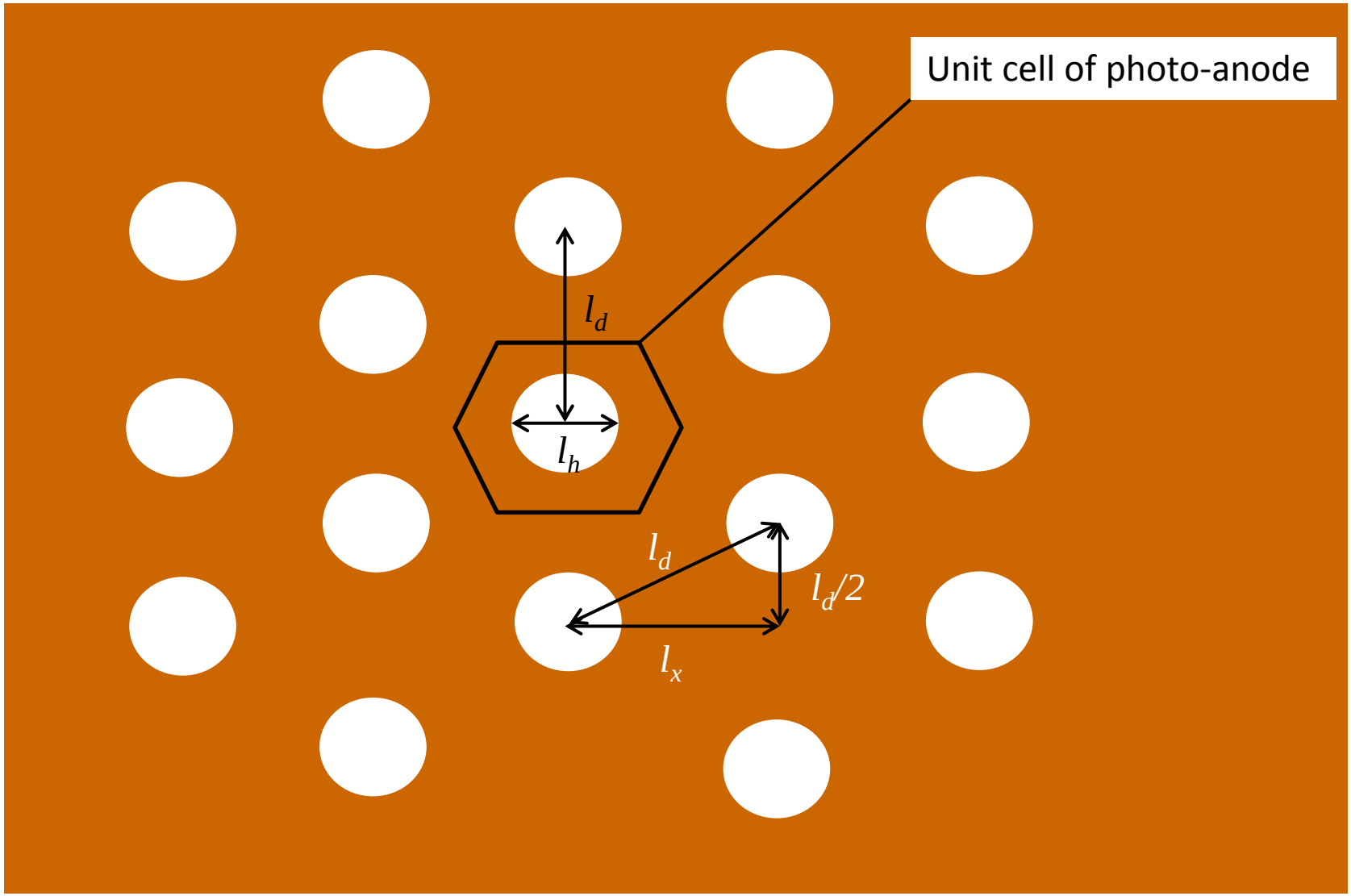
Predicted Spatial Distribution of O_2 Secondary Current Density at 0.1×0.1 m^2 Ti |Sn^{IV}-Fe_2O_3 (Back-side) Anode in 1 M NaOH solution (pH ca. 13.7); Ti | Pt cathode

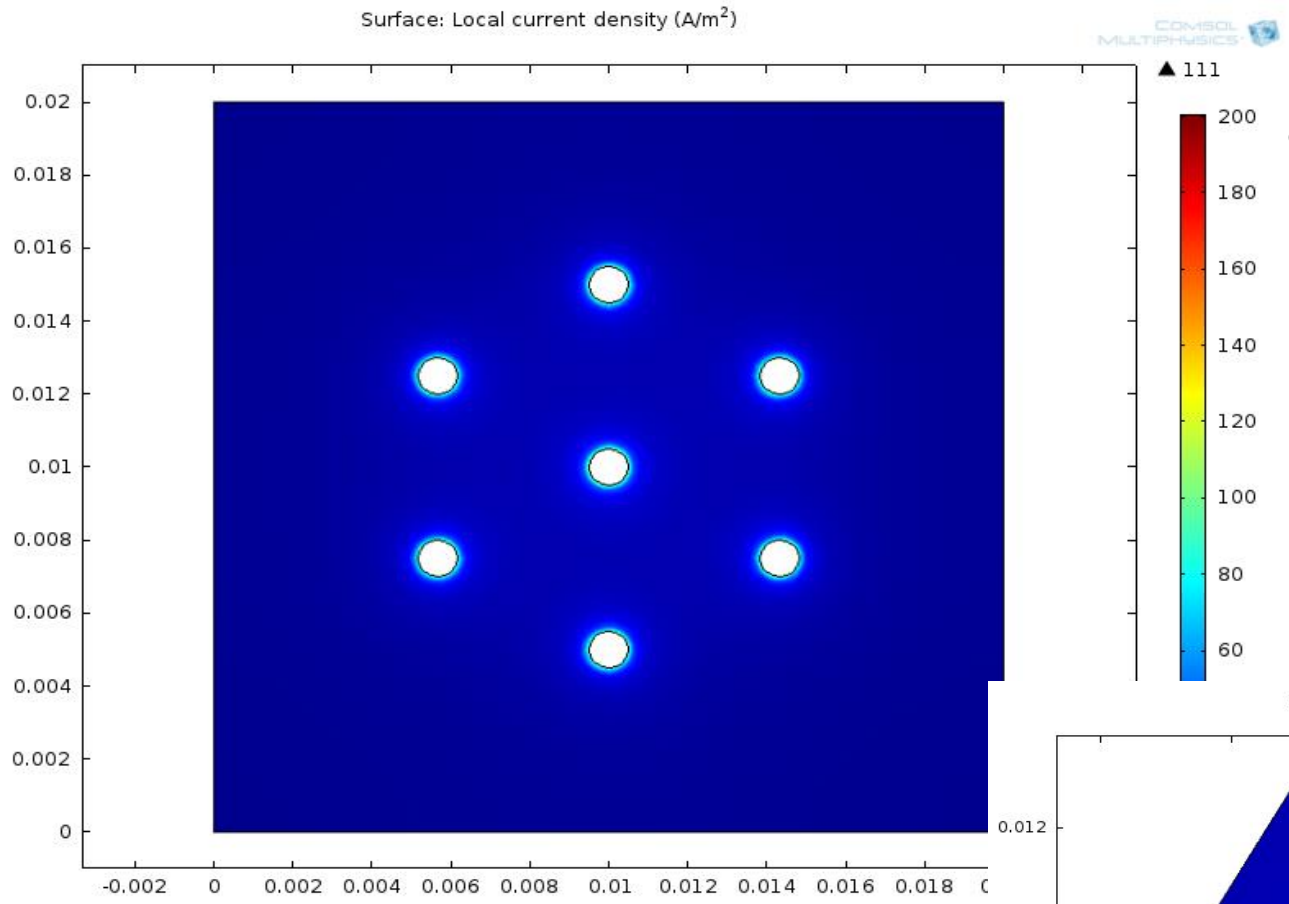


Geometry of Perforated Ti / Sn^{IV}-doped Fe_2O_3 Photo-anode

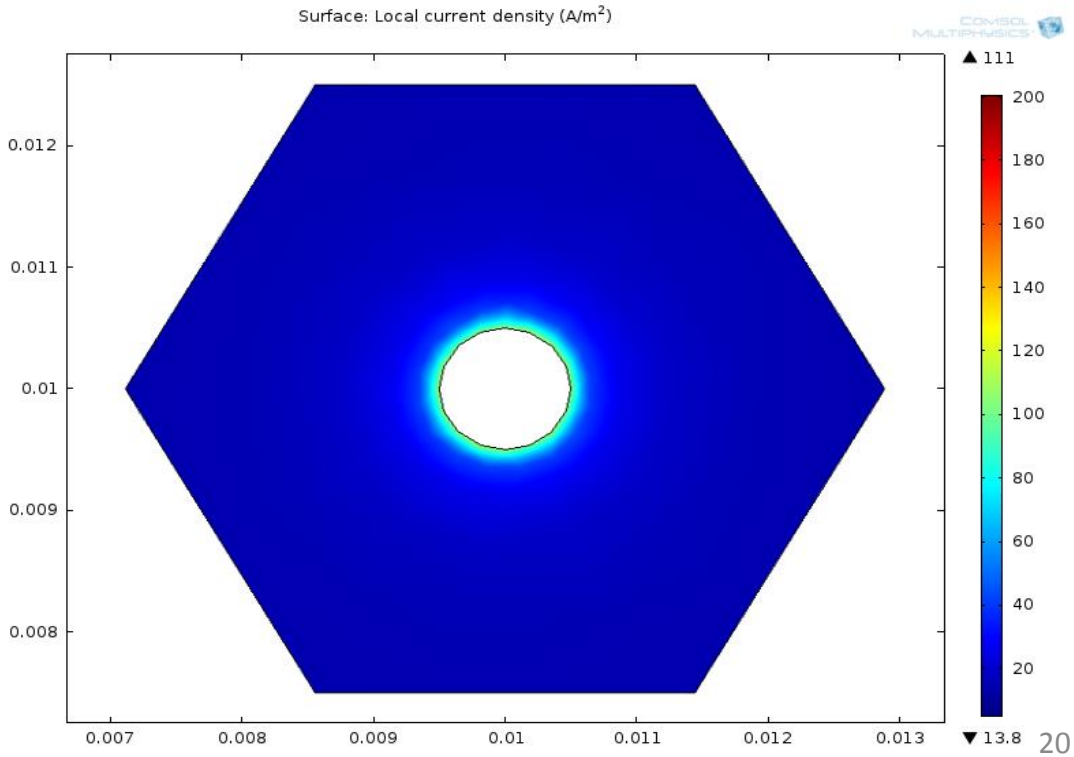
Is there an optimal geometry for perforations?

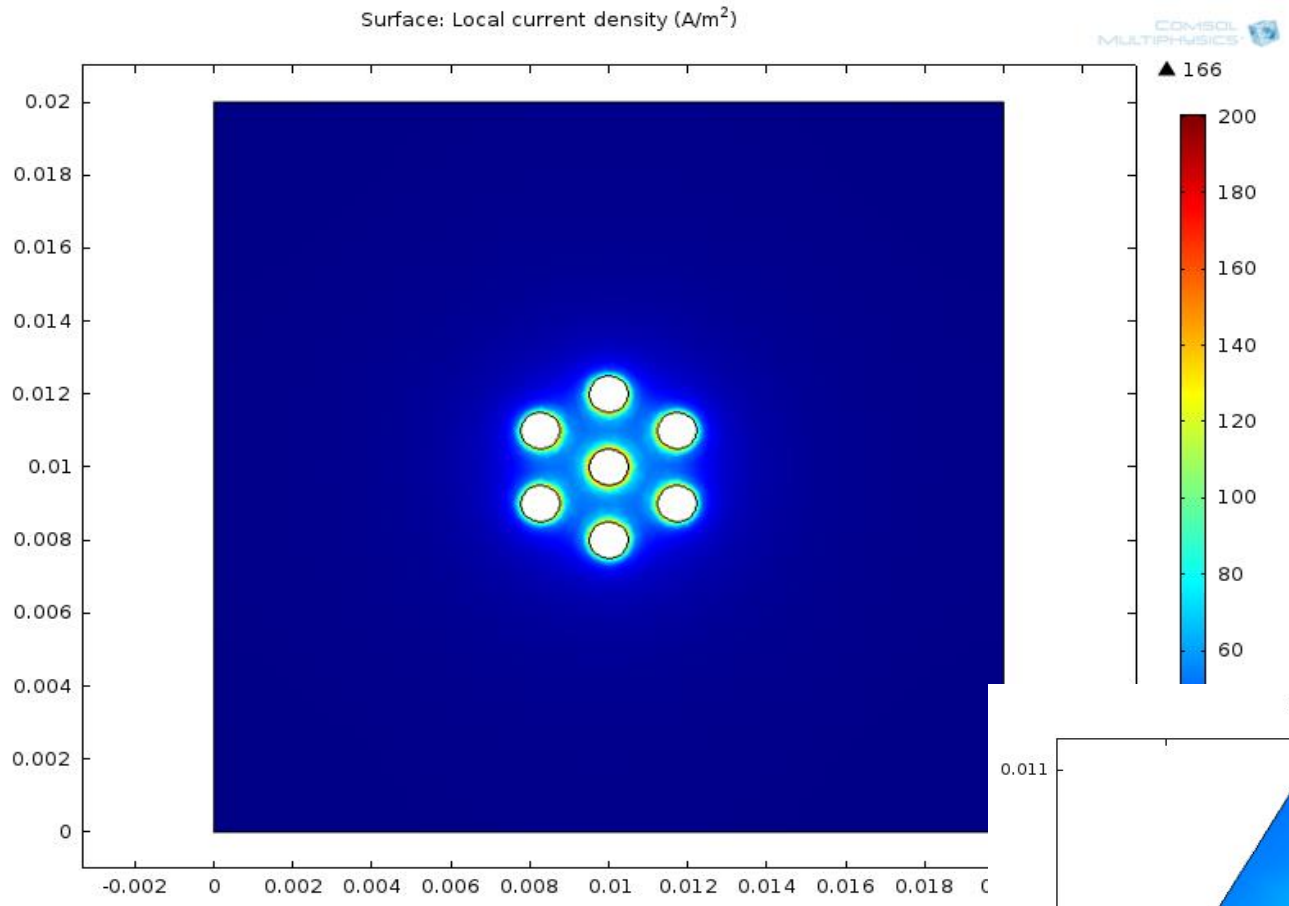
Ionic current paths homogenise current distribution, but lose photo-active area



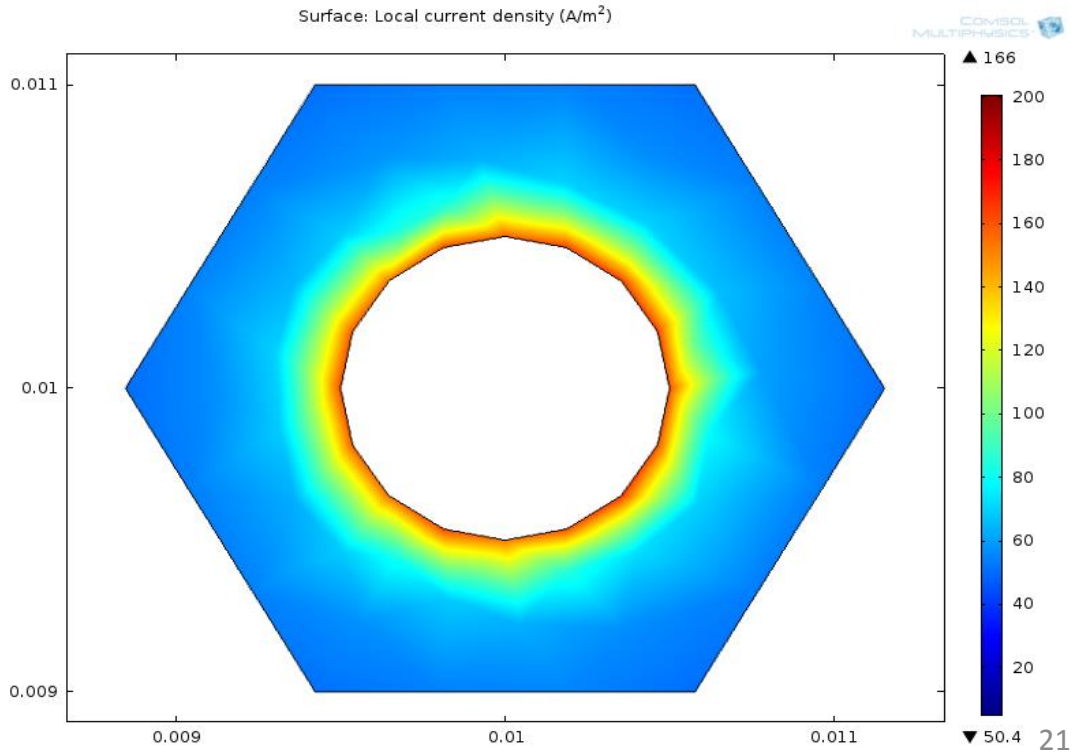

Surface: Local current density (A/m²)
▲ 111
200
180
160
140
120
100
80
60
Current density / A m-2
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018

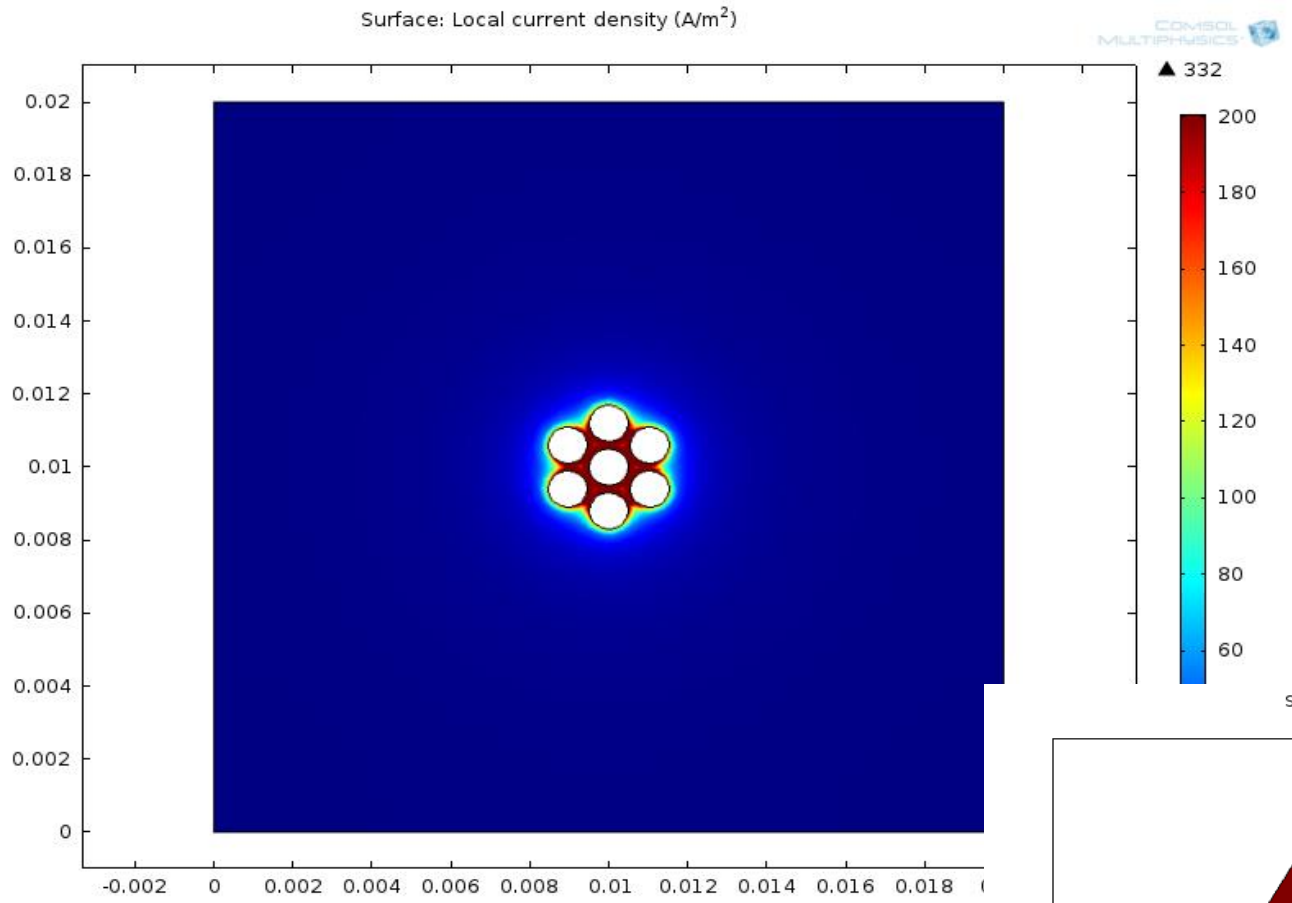
$$\frac{l_d}{l_h} = 5$$


Surface: Local current density (A/m²)
▲ 111
200
180
160
140
120
100
80
60
40
20
▼ 13.8
0.012
0.011
0.01
0.009
0.008
0.007
0.008
0.009
0.01
0.011
0.012
0.013

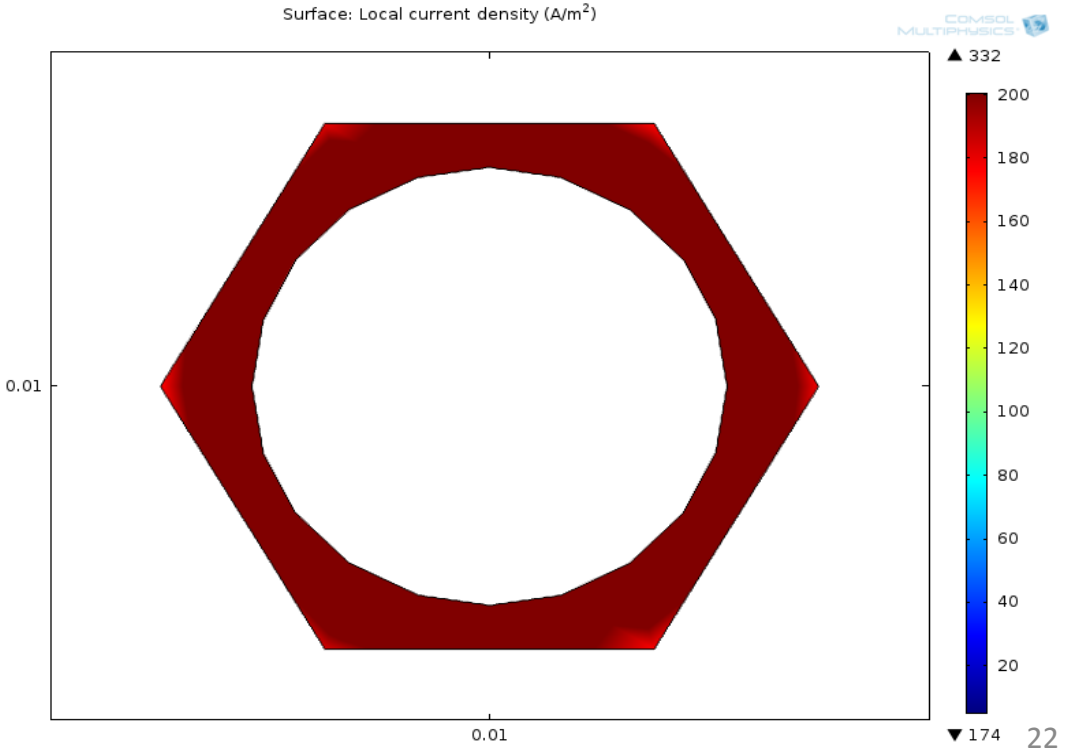

Surface: Local current density (A/m²)
▲ 166
200
180
160
140
120
100
80
60
Current density / A m-2
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018

$$\frac{l_d}{l_h} = 2$$

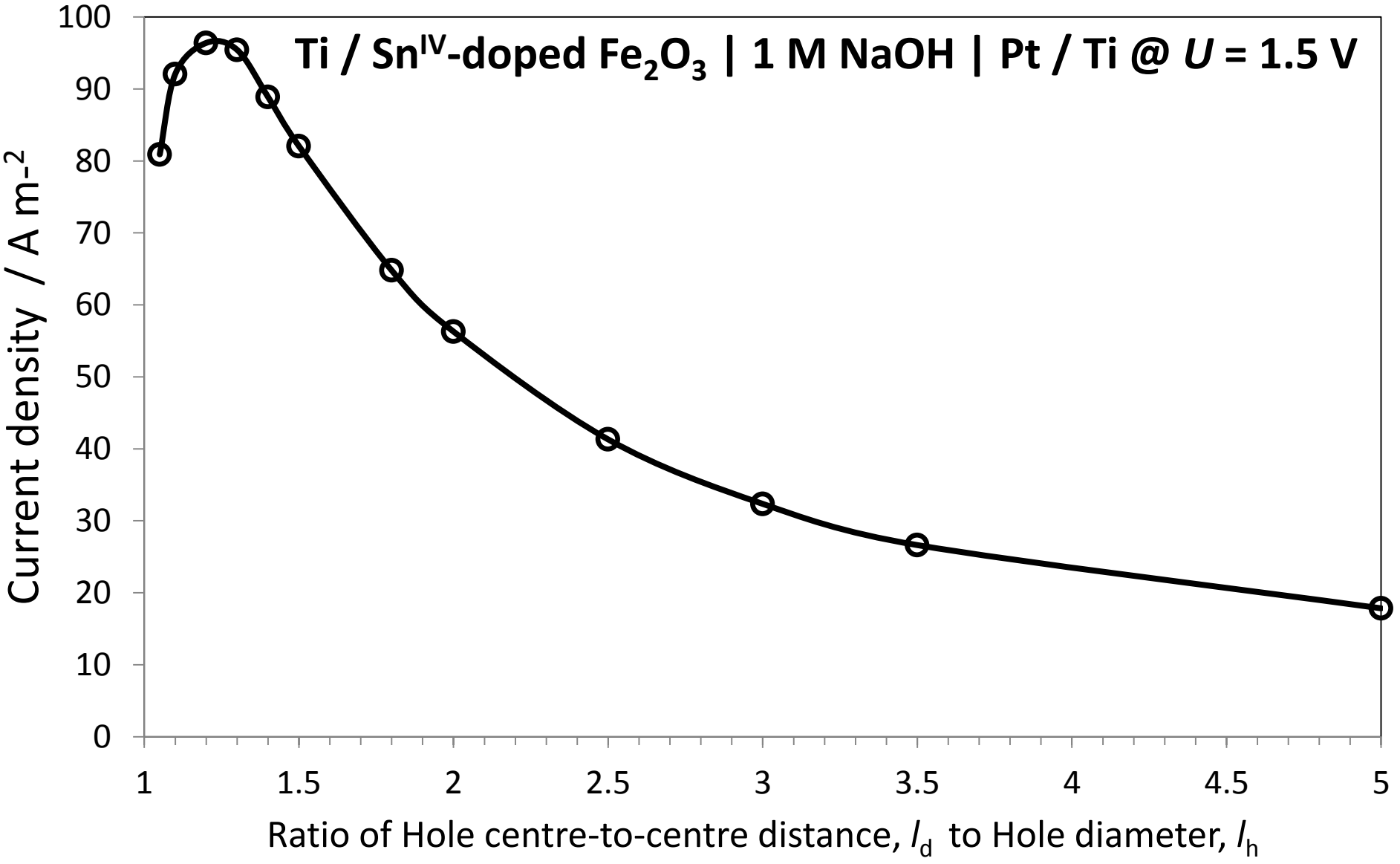

Surface: Local current density (A/m²)
▲ 166
200
180
160
140
120
100
80
60
40
20
▼ 50.4
0.011
0.01
0.009
0.009
0.01
0.011


Surface: Local current density (A/m²)
▲ 332
200
180
160
140
120
100
80
60
Current density / A m-2
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018

$$\frac{l_d}{l_h} = 1.2$$


Surface: Local current density (A/m²)
▲ 332
200
180
160
140
120
100
80
60
40
20
▼ 174
0.01
0.01

Effect of Ratio of Hole Centre-to-centre Distance to Hole Diameter on (Geometric) Anode Current Density



Summary

- (Sn^{IV}-doped) Fe_2O_3 photo-anodes produced on F-doped SnO_2–coated glass or metal substrates by spray-pyrolysis.
- Fe_2O_3 photo-anode | anolyte| membrane | catholyte | cathode photo-assisted electrolyser produced current densities of 1-10 A m^{-2} ($\approx (0.5 - 5)\times 10^{-5}$ mol H_2 m^{-2} s^{-1}).
- Current densities of photo-electrochemical reactor with Fe_2O_3 photoanode increased linearly with photon flux.
- Models well predict distributions of potential, current densities, dissolved gas, and photocurrent densities as *f*(light intensity).

Power Challenge

World power consumption of ca. 14 TW in 2010 predicted to double by 2050

Incident Solar Power

- 125,000 TW at earth's surface
- 36,000 TW on land

$$\text{Photo-electrochemical Area, } A_{photon} \ / \ \mathrm{m}^2 \cong \frac{1.4\times10^{13}\left(\mathrm{W}\right)}{\Phi^{e}_{\text{photon}}\times170\left(\mathrm{W\,m^{-2}}\right)} \cong \frac{8.2\times10^{10}\left(\mathrm{m}^2\right)}{\Phi^{e}_{\text{photon}}}$$

Global mean irradiance

Photon yield

Photo-electrode requirements:

- Efficient
- Cheap
- robust

} Any 2 of 3 properties possible at present

+ easily fabricated on large scale

Solubility (activity-pH) diagram for Fe_2O_3 (c)

in equilibrium with aqueous Fe^{III} species at 298 K