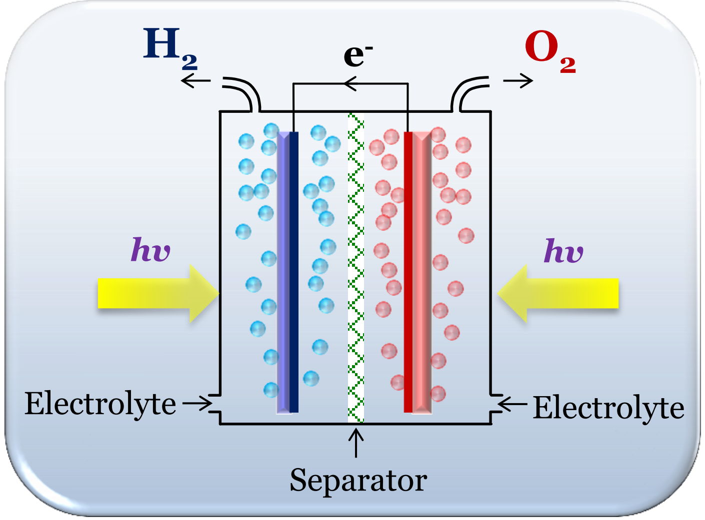
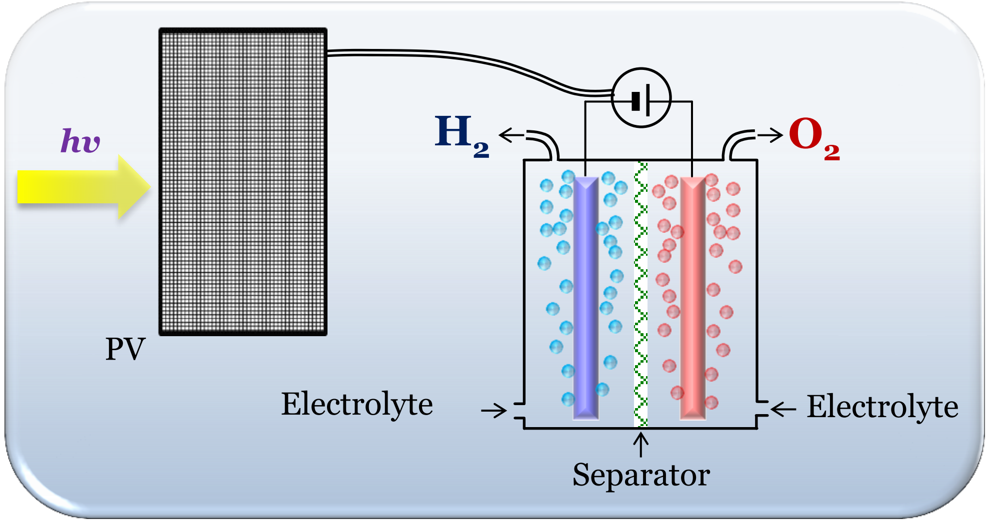
Imperial College London

Comparing 'photo-electrochemical' and 'electrochemical-powered-by-PV' systems for solar H_2O splitting

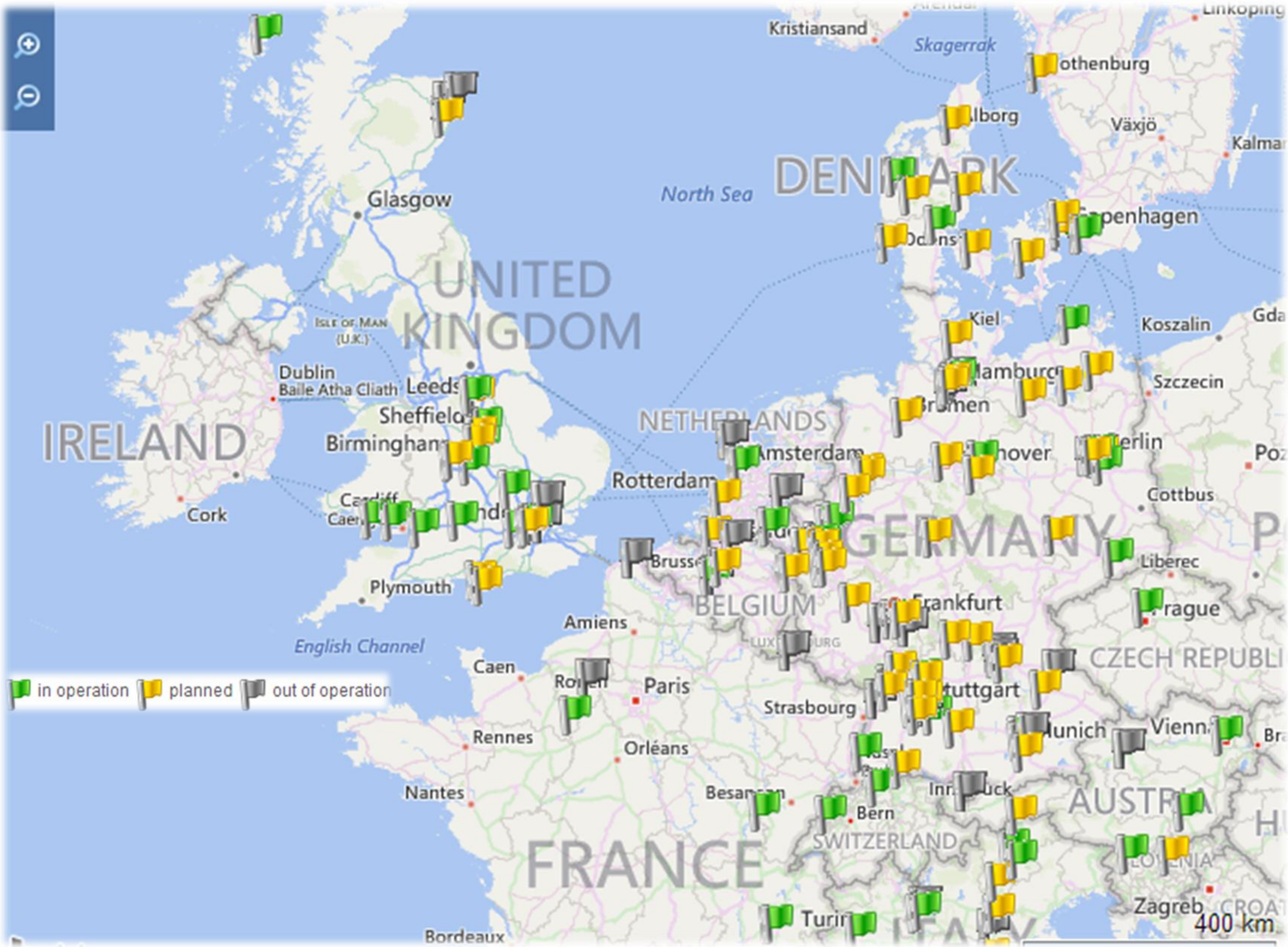




Solar Fuels Symposium
Imperial College London
10 December 2014

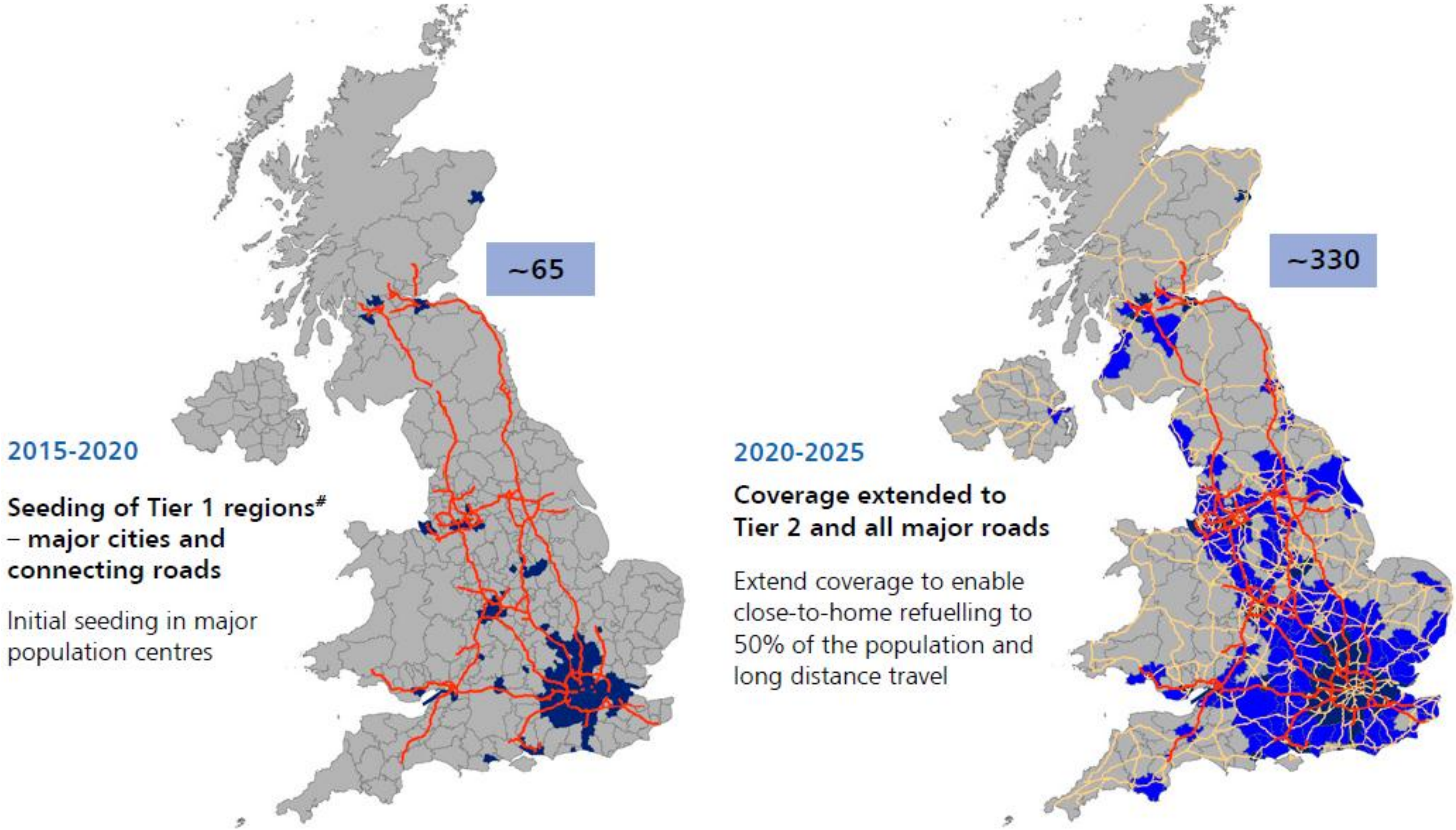
Dr Anna Hankin
anna.hankin@imperial.ac.uk
Postdoctoral Research Associate
Electrochemical Engineering Research Group

Current & prospective H_2 refuelling stations in the UK & Europe



UK H_2Mobility project: an opportunity for solar?

UK H_2Mobility mapped out the hydrogen refuelling station (HRS) network development in the UK over the period from 2015 to 2030. An initial network of 65 HRS in 2015 will need to develop and expand to meet hydrogen demand from a growing fleet of FCEVs through to 2030.



PV + Electrolyser operation

- Solar Photons
- *PV*
- Electrical Energy
- Electrolyser
- H_2 + O_2 gases
- Fuel Cell
- Electrical Energy
- Electrical Appliance / Motor

Solid State Device with a p-n junction

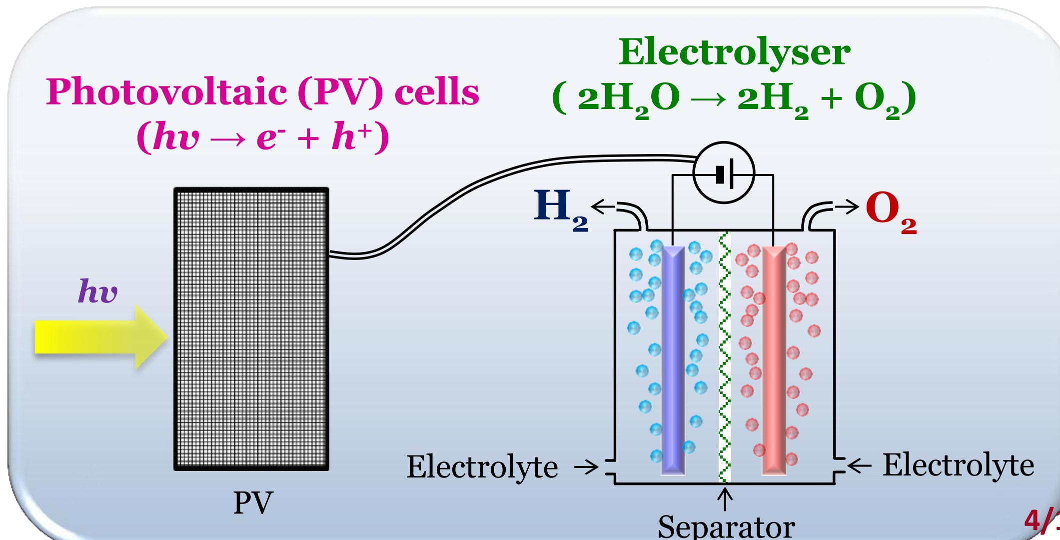
Function of PV device:

- Absorption of photons
- Generation of electrical charge and current

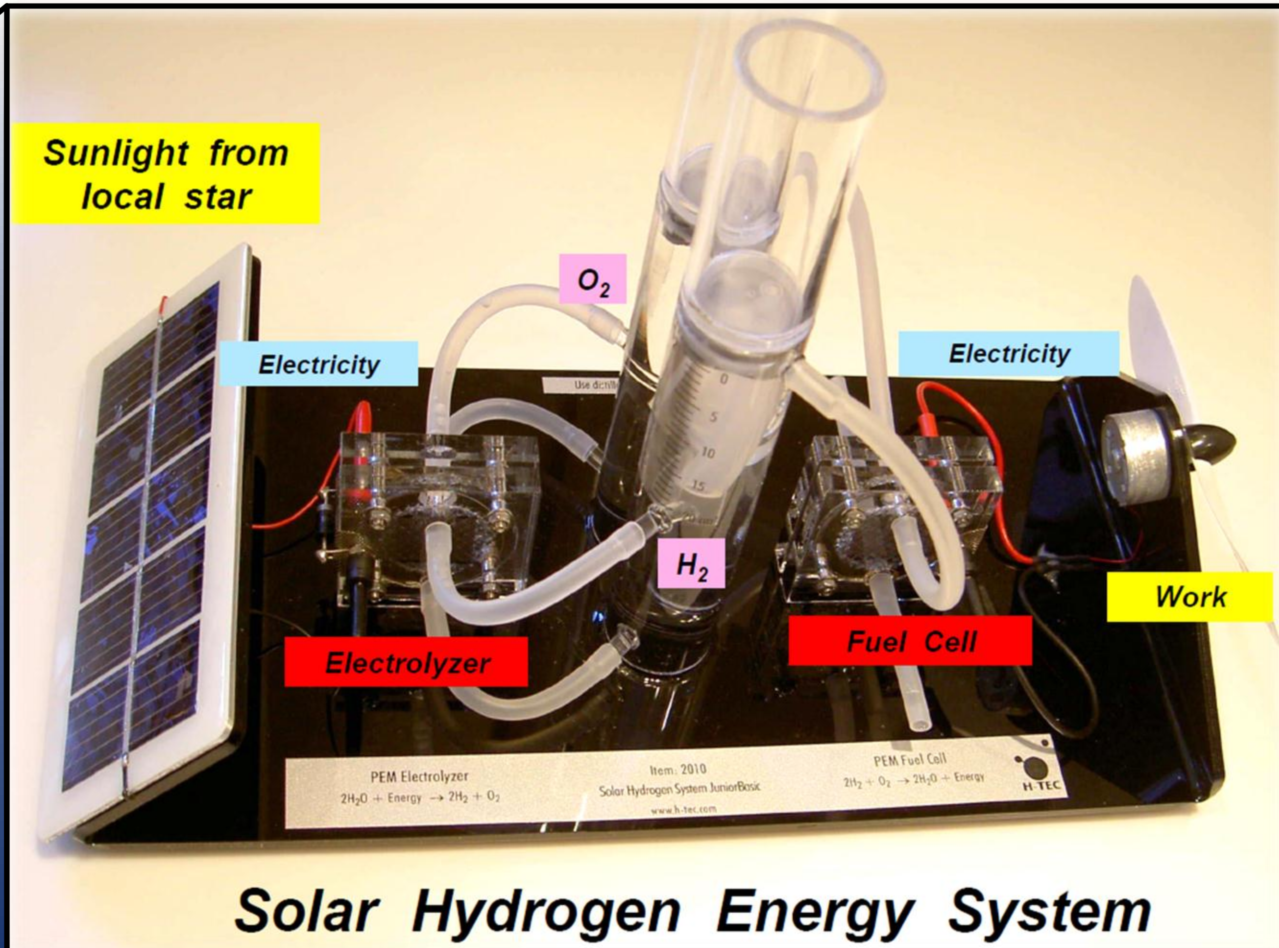
Electrochemical Reactor

Function of Electrolyser:

- Two electrodes immersed in an electrolyte generate H_2 and O_2, respectively when
- Current or voltage is applied between them (this could come from PV)



Solar energy storage in fuel



Blades of electric fan spin when PV is illuminated by the Sun

‘Junior Basic’ Renewable Energy Demo

Demo presented by Bill Leighty, *NH_3 Fuels Association, http://leightyfoundation.org*

Photo-electrochemical reactor

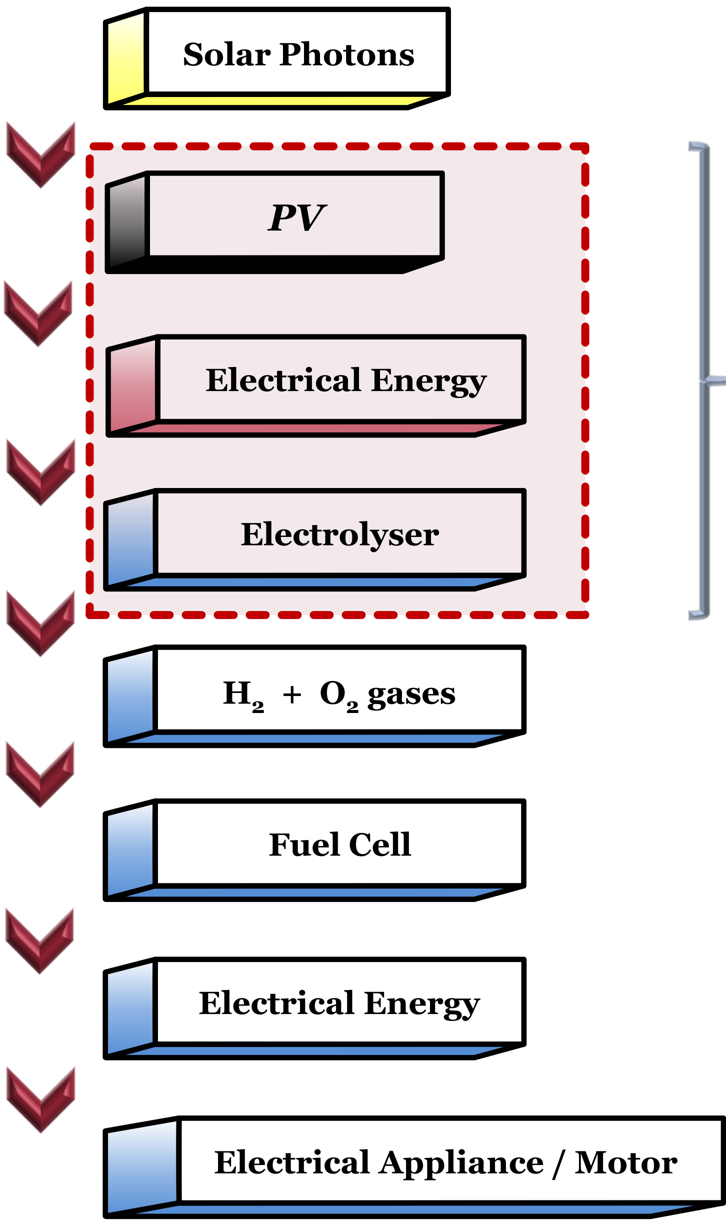
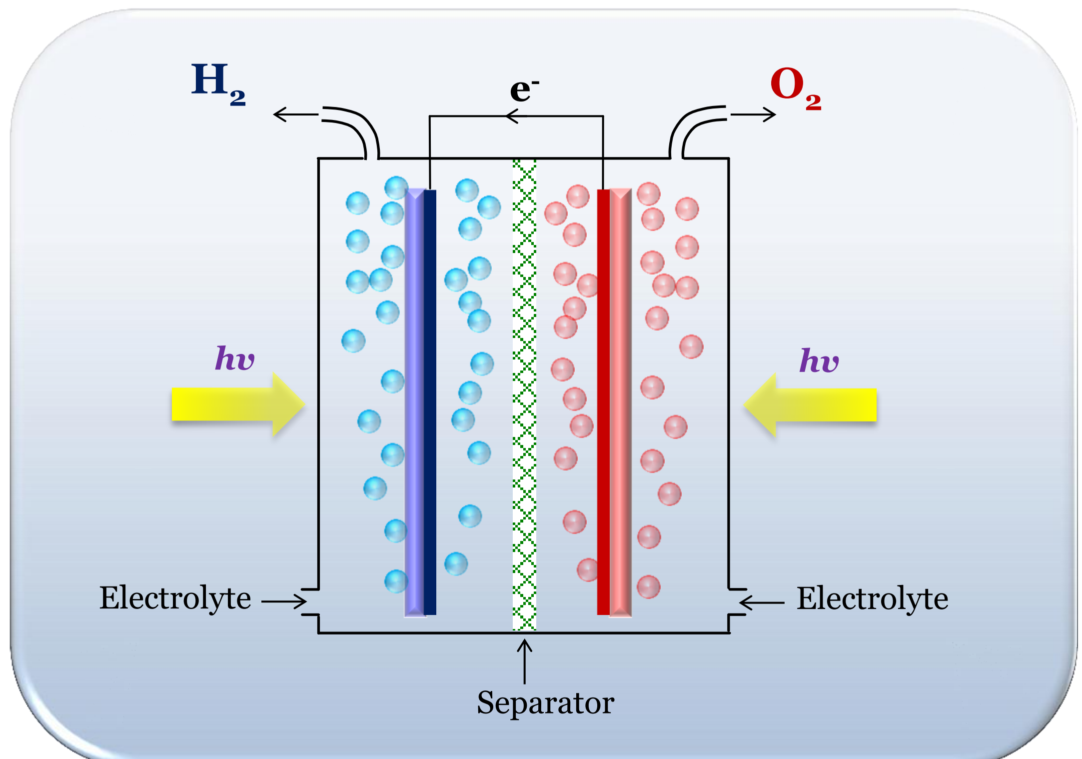
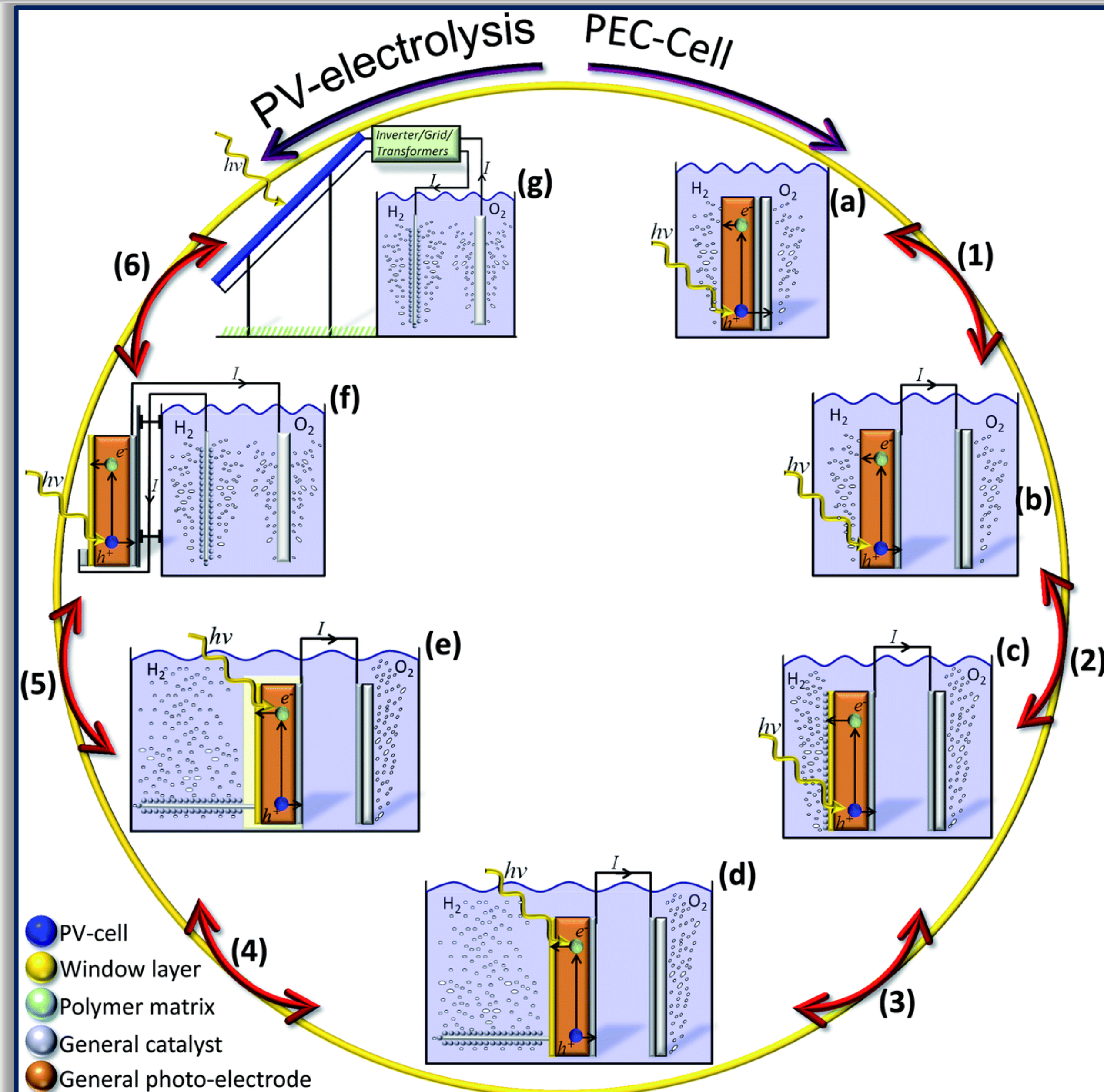


Photo-electrochemical Reactor

- Photo-electrodes function as photo-absorbers and catalysts simultaneously
- Wired structure shown; wireless ‘diode’ structures also possible



Are the two systems inherently different?



It has been argued that the core processes of:

- Photon absorption
- Charge separation
- Charge transport
- Catalysis

and the order in which they occur in the two systems are the same. Hence, the two systems are inter-convertible and differ only in the "spatial relation between the core functionalities".

T.J. Jacobsson et al., *Energy Environ. Sci.* 2014, 7, 2056

Key factors in the choice between 'photo-electrochemical' & 'PV+electrolyser' configurations

- **Which is easier to illuminate?**
- **Effort required to produce a good photo-absorber stable in solution?**
- **Does the protective coating cause too much attenuation ?**

PEC

Stability

- Extremely pH sensitive

Device design (electrode geometry)

- Dictated by semiconductor deposition strategy. Usually limited to planar geometry.

Amount of material

- Extra protective coating required to stabilise the photo-absorber in solution and to provide catalytic effect.

PV + electrolyser

Stability

- Catalyst can be easily tailored to electrolyte

Device design (electrode geometry)

- Flexible if catalyst bulk is same material as catalyst surface.

Amount of material

- Extra length of conductor required to connect externally mounted PV to the working electrode

H_2 Fuel Cell Electric Vehicles (FCEVs)

Honda FCX Clarity

- H_2 tank pressure = 350 bar
- H_2 tank volume = 170 dm³
- H_2 mass in full tank = 4.8 kg
- Driving range / charge = 386 km

Hyundai ix35

- H_2 tank pressure = 700 bar
- H_2 tank volume = 100 dm³
- H_2 mass in full tank = 5.6 kg
- Driving range / charge = 594 km

Microcab

- H_2 tank pressure = 350 bar
- H_2 tank volume = 26 dm³
- H_2 mass in full tank = 2.5 kg
- Driving range / charge = 289 km

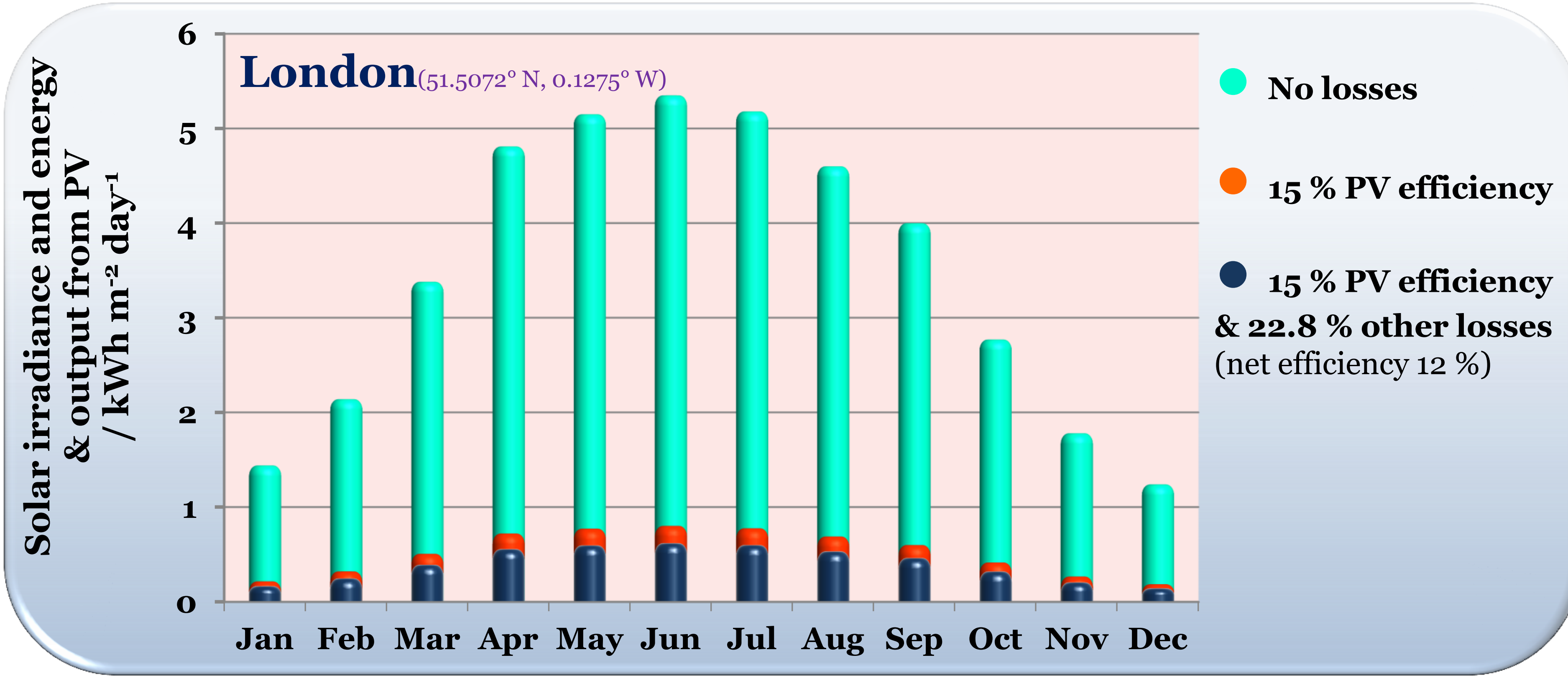
Mercedes B-Class F-CELL

- H_2 tank pressure = 700 bar
- H_2 tank volume = 65 dm³
- H_2 mass in full tank = 3.7 kg
- Driving range / charge = 385 km

Lotus Hydrogen Fuel Cell Taxi

- H_2 tank pressure = 350 bar
- H_2 tank volume = 131 dm³
- H_2 mass in full tank = 3.7 kg
- Driving range / charge = 257 km

Solar energy & PV efficiency

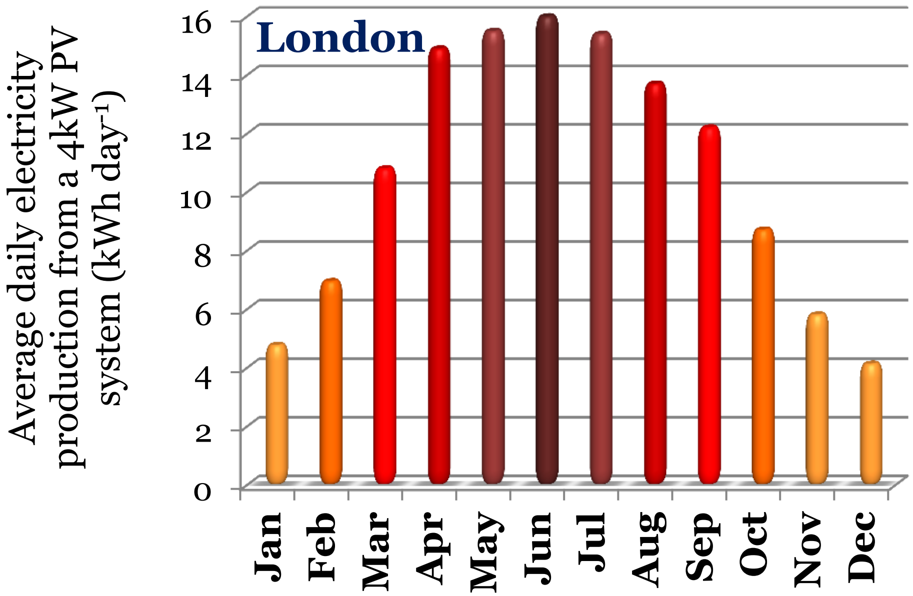


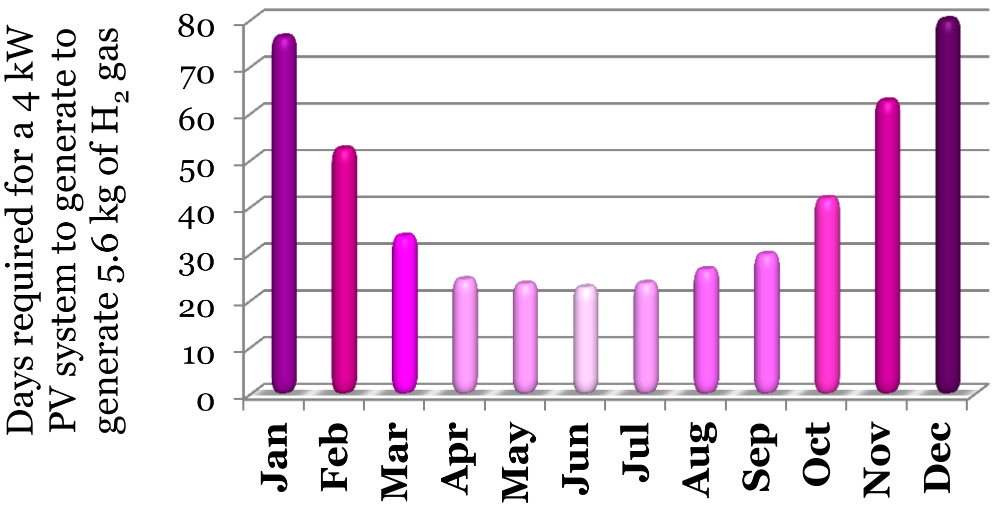
Yearly averages (London):	**1280 kWh m^{-2} year^{-1}**
	$\Rightarrow$ 150 W m^{-2} hr^{-1} (average day & night)
	$\Rightarrow$ 22 W m^{-2} hr^{-1} (average based on 15 % efficiency)

Data obtained using: PVGIS online software (Online free solar photovoltaic energy calculator for stand alone or connected to the grid PV systems and plants, in Europe and Africa)

Hydrogen Refuelling at Home

In UK, the maximum permissible domestic PV installation = 4 kW (ca. 16 PV panels)





- **High pressure alkaline electrolyser requires ca. 65 kWh kg(H_2)$^{-1}$ (@ 350 bar) (*Hydrogenics*)**

⇒ **Producing 59.7 kg solar H_2 per year**

⇒ **Re-fuelling a 5.6 kg H_2 tank only 11 times**

⇒ **Maximum travel distance 6,332 km or 3,935 miles year^{-1}**

H_2 FCEVs vs. fully electric vehicles

BMW i3

- Mean driving range / charge = 160 km
- eDrive energy consumption = 12.9 kWh / 100 km
- Li-ion battery capacity = 19 kWh
- A 4kW PV system will recharge the car 204 times year^{-1}

=> Annual travel distance ≈ 32,674 km (20,303 miles)

Vauxhall Ampera

- Mean driving range / charge = 38miles (avg.)
- Li-ion battery (smallest) capacity = 16 kWh
- A 4kW PV system will recharge the car 243 times year^{-1}

=> Annual travel distance ≈ 14,830 km (9,215miles)

Tesla Model S

- Mean driving range / charge = 244 miles
- Li-ion battery (smallest) capacity = 60 kWh
- A 4kW PV system will recharge the car 65 times year^{-1}

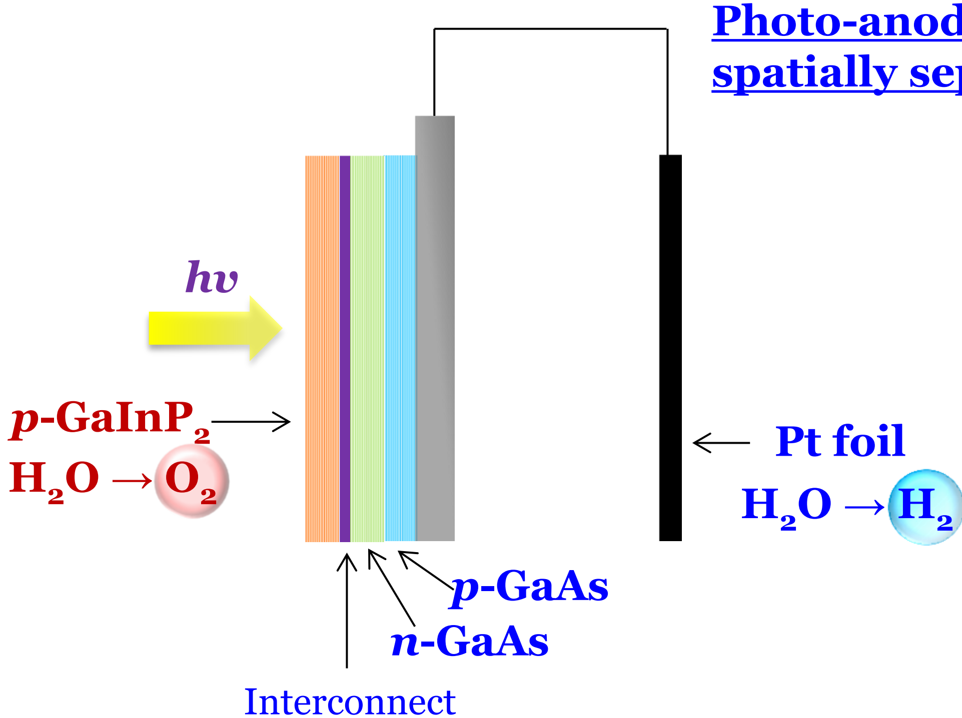
=> Annual travel distance ≈ 25,393 km (15,779 miles)

Total energy generated per year by an optimally inclined 4 kW PV system in London = 3,880 kWh

Monolithic integrated Ga-based PV-PEC cells

Turner group (NREL, Colorado): O. Khaselev & J.A. Turner, *Science*, 1998, 280, 425

Photo-anode & cathode spatially separated



- **Current density = 1,200 A m^{-2} (11 suns) => ≈ 90 A m^{-2} (1 sun, AM 1.5)**
  => ≈ 1.68 mol(H_2) hr^{-1} m^{-2}
  => ≈ 3.36 g(H_2) hr^{-1} m^{-2}
- **PEC solar to H_2 efficiency = 12.4 %**

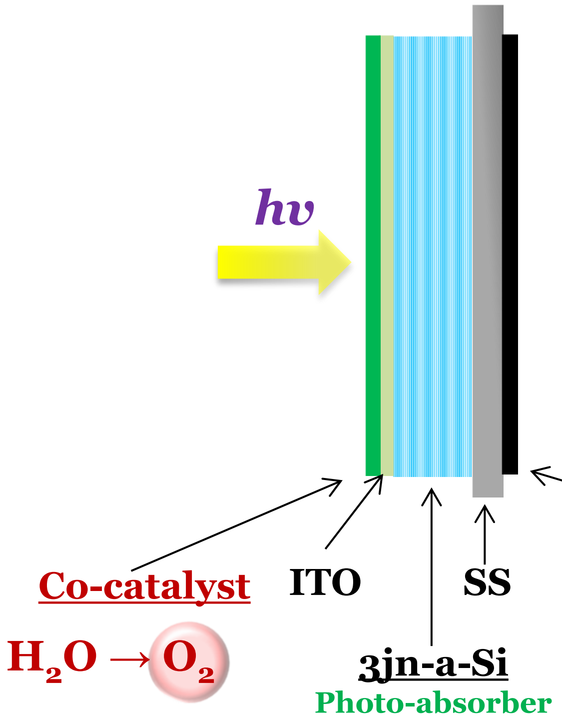
Problem: Poor potential and current distribution; GaAs, GaInP$_2$ unstable

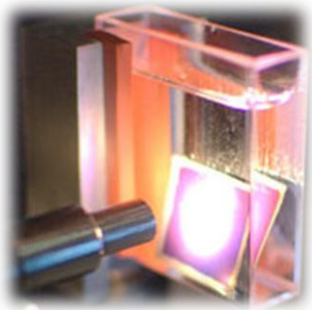
Catalysed triple junction amorphous silicon cells

D.G. Nocera group:

S.Y. Reece et al., *Science*, 2011, 334, 645
D.G. Nocera, *Acc. Chem. Res.*, 2012, 45, 767

Monolithic

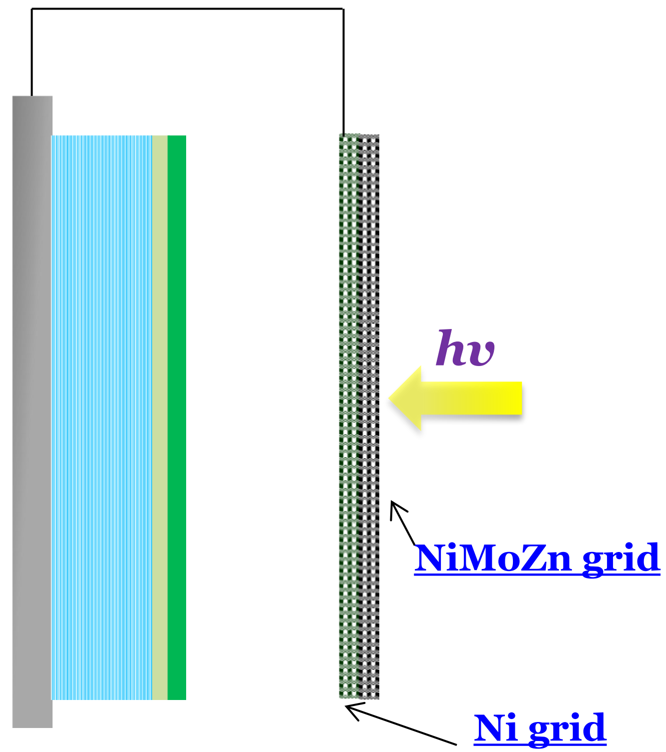




- PV efficiency = 6.2 %
- PEC solar to H_2 efficiency = 1.75 %
- 1 M K_3BO_3 electrolyte, pH 9.2

Problem: Poor potential and current distribution

Electrodes separated

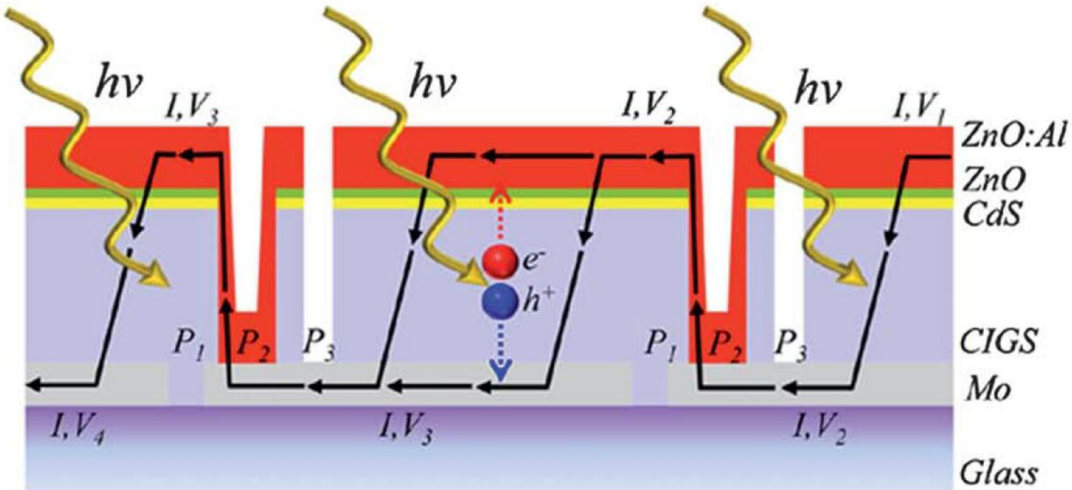


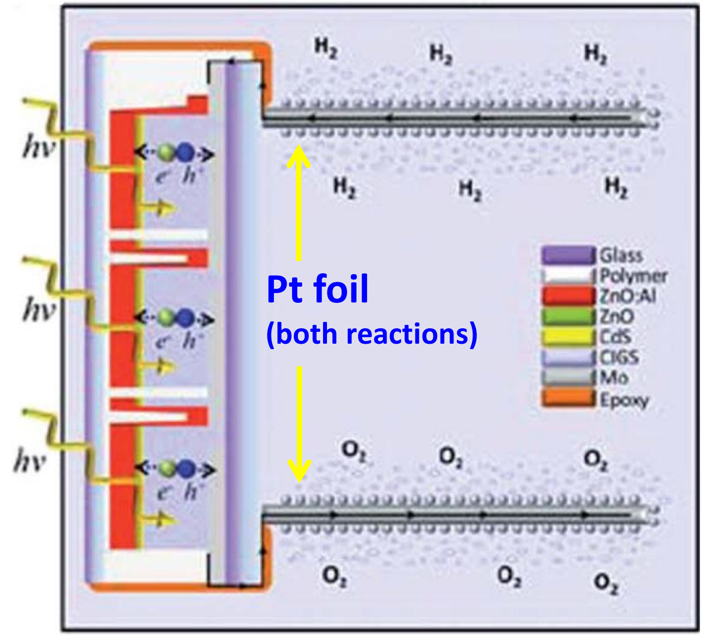
- PV efficiency = 7.7 %
- Electrolysis efficiency = 61 %
- PEC solar to H_2 efficiency = 4.7 %
- 1 M K_3BO_3 electrolyte, pH 9.2
- Uniform potential and current distribution

CIGS-based monolithic interconnected cells

T. Edvinsson group: T.J. Jacobsson et al., *Eng. Environ. Sci.*, 2013, 6, 3676
T.J. Jacobsson et al., *Eng. Environ. Sci.*, 2014, 7, 2056

Monolithic





- 3 CIGS ($CuIn_xGa_{1-x}Se_2$) cells connected in series
- Combined 3 cell PV efficiency = 17 %
- PEC solar to H_2 efficiency = 10 % (at 1 sun)
- Current density ≈ 82 A m^{-2}
- Rate of H_2 production ≈ 56.5 dm^3 hr^{-1} m^{-2} => 5.6 g(H_2) hr^{-1} m^{-2} (at 1 atm.)

Problem: H_2 & O_2 gases are evolved in one compartment, so require subsequent separation

Conclusions

- **Coupled PV-electrolyser systems hold strong advantages over photo-electrochemical systems:**
  - No need for protective coatings
  - Minimal semiconductor stability problem
  - Absorption / reflection losses eliminated
  - Broader range of electrolytes is available
  - Catalyst can be synthesized, tested and optimised separately from the photo absorber

- **However, it is not practical to refuel vehicles with H_2 produced using energy only from coupled PVs + Electrolysers due to very low H_2 production rates**

- **Efficiencies of small-scale photo-electrochemical reactors comfortably match those of coupled PV-electrolyser systems, encouraging further work in this field and projects for device scale-up**

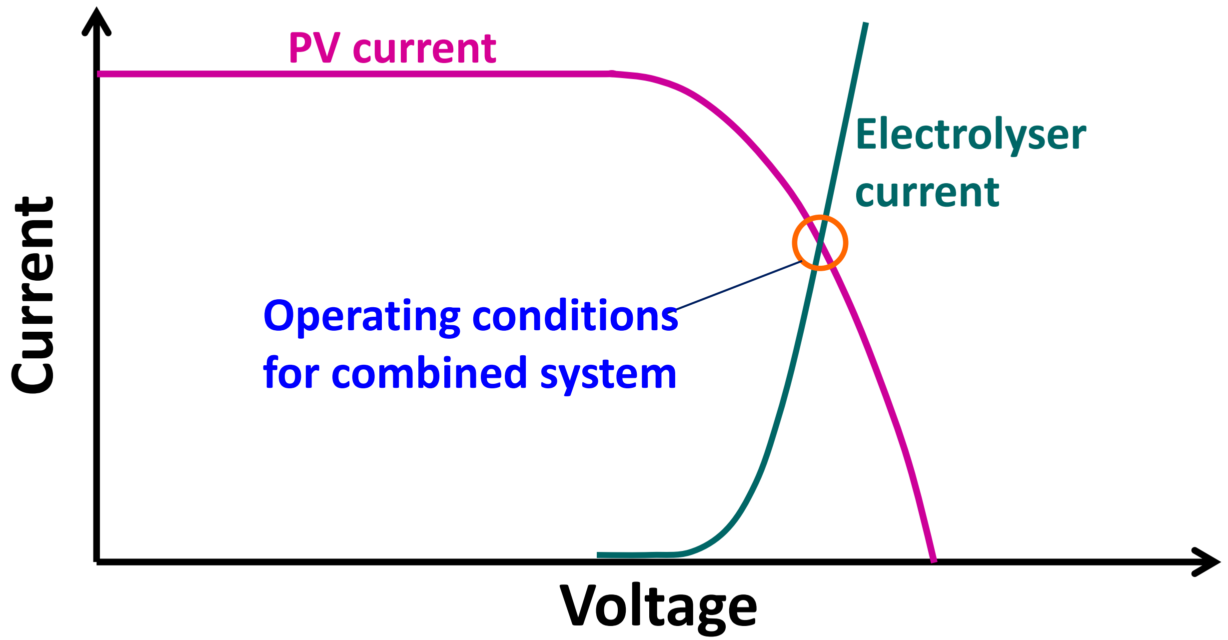
THANK YOU!

Q & A

SUPPORTING SLIDES

Coupling PVs with Electrolysers: A Practical Demo

To determine the performance of the combined system the PV and Electrolyser entities must first be characterised in terms of I-V performance separately:



$$\text{Solar to } H_2 \text{ system efficiency [1]} = \text{Maximum PV efficiency [1]} \times \text{Electrolyser operational efficiency [1]} \times \text{Coupling factor [1]}$$

$$\text{Coupling factor [1]} = \frac{\text{PV power achieved [W]}}{\text{Maximum PV power [W]}}$$

Operational Hydrogen Refuelling Stations in the UK

Loughborough Hydrogen Vehicle Refuelling Station
Services passenger cars
Refuelling pressure: 350 bar

University of Birmingham
Services passenger cars
Refuelling pressure: 350 bar
http://www.birmingham.ac.uk/research/facilities/hydrogen-fuel.aspx

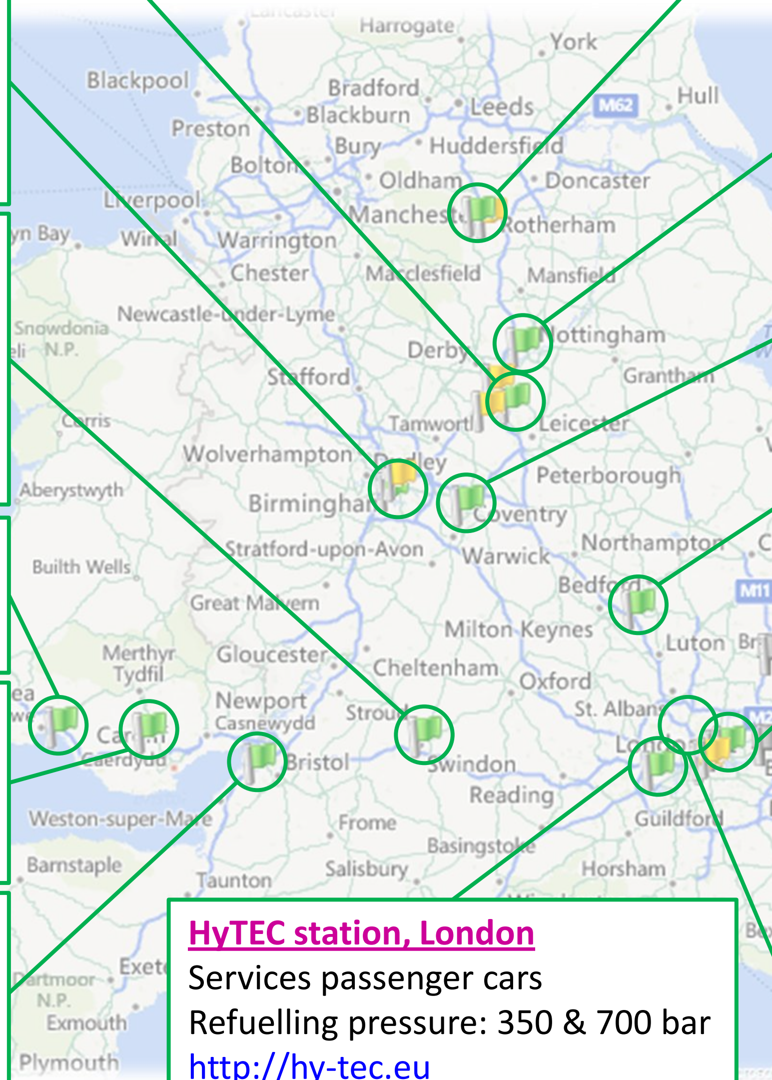
Honda Manufacturing Station, Swindon
Services passenger cars (4 / hour)
Refuelling pressure: 700 bar
http://www.hyfive.eu/the-hyfive-project/#refuel

Hydrogen Research and Demonstration Center, Port Talbot
Refuelling pressure: 350 bar

University of Glamorgan
Services passenger cars
Refuelling pressure: 350 bar
www.h2wales.org.uk

Hydrogen Ferry Demonstration Project, Bristol
Refuels boats
www.bristolhydrogenboats.co.uk

H2 SEED Facility: Hebridean Hydrogen Park
www.hi-energy.org.uk



ITM Power Green Hydrogen Refuelling Station, Sheffield
Source of H_2 = electrolysis
Refuels passenger cars
H_2 tanks at 350 bar
www.itm-power.com

Midlands Hydrogen ring, Nottingham
Services passenger cars
Refuelling pressure: 350 bar

Coventry University Station
Services passenger cars
Refuelling pressure: 700 bar

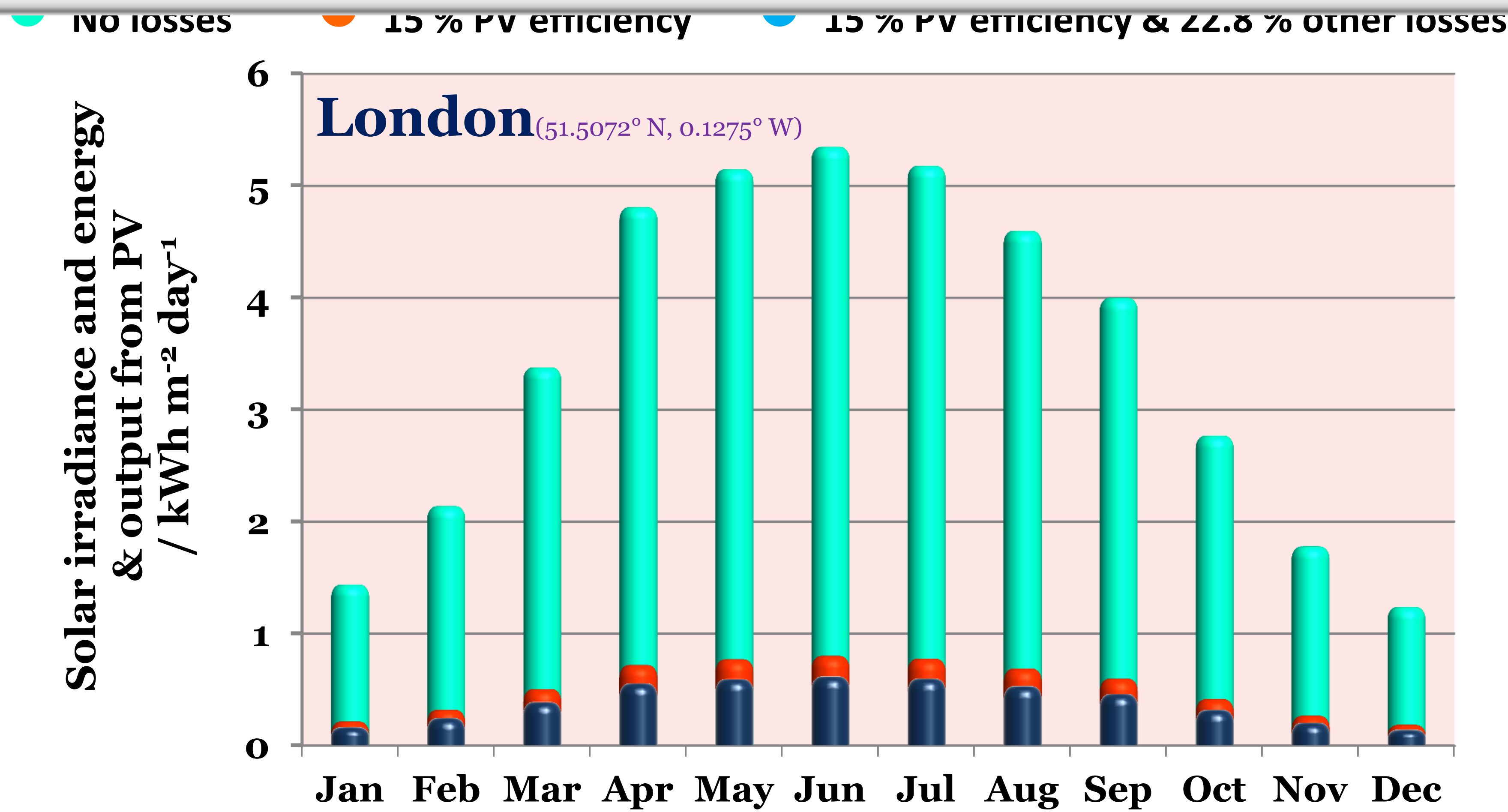
London Bedford station
Services passenger cars and buses
Refuelling pressure: 350 bar

LHP London Hydrogen Partnership CHIC project
Services passenger cars and buses
Refuelling pressure: 350 bar
http://www.hydrogenlondon.org/

HyFIVE station, Hillingdon
Services passenger cars
Refuelling pressure: 350 & 700 bar
http://www.hyfive.eu/the-hyfive-project/#refuel

HyTEC station, London
Services passenger cars
Refuelling pressure: 350 & 700 bar
http://hy-tec.eu

Solar Energy & PV Efficiency



Yearly averages (London): **1280 kwh m^{-2} $year^{-1}$**

$\Rightarrow$ 150 W m^{-2} hr^{-1} (average day & night)

$\Rightarrow$ 22 W m^{-2} hr^{-1} (average based on 15 % efficiency)

Data obtained using: PVGIS online software (Online free solar photovoltaic energy calculator for stand alone or connected to the grid PV systems and plants, in Europe and Africa)

Complications of Photo-Electrochemical Reactors

- **Often good solar light absorbers demonstrate poor:**
  - Catalytic activity
  - Stability in aqueous solutions

- **This imposes a need for additional coatings to be applied to the photo-absorbers which:**
  - Increase fabrication complexity
  - Increase fabrication & capital costs
  - Result in light attenuation, thereby reducing the quantum efficiency

  And require
  - Appropriate band edge / Fermi levels
  - Good charge transport properties
  - Good stability

- **Illumination of electrodes can be hindered by the production of bubbles**

Degradation of an unprotected CIGS solar cell:

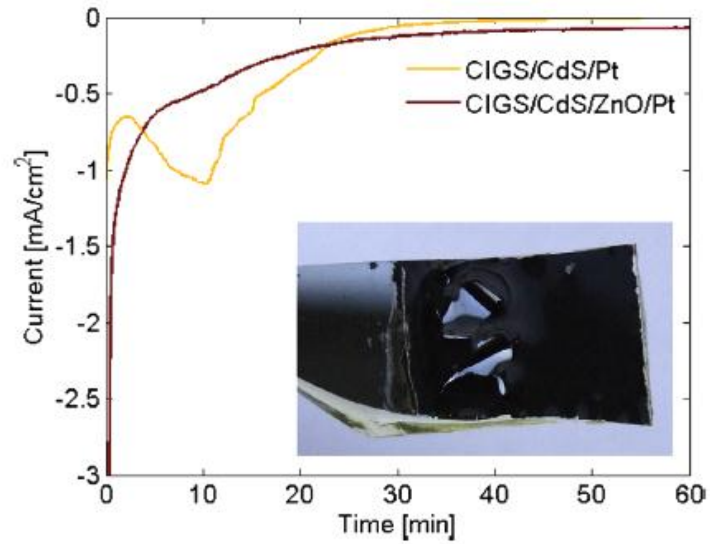
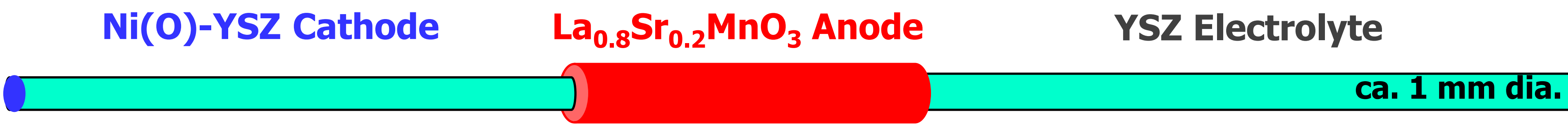


Fig. 3 – (a) Photocurrent under simulated AM 1.5 illumination at −0.4 V vs. NHE for samples of CIGS/CdS/Pt and CIGS/CdS/ZnO/Pt. The inset illustrates the macroscopic degradation of one of the films.

T.J. Jacobsson et al., *Int. J. Hyd. Eng.*, 2013, 38, 15027

Solid Oxide Electrolysers: Great Improvement?

Micro-tubular solid oxide electrolyser:



A single fiber has an electroactive area of ca. 0.4 cm^2

This electrolyser is able to generate:

- Current density of 5 kA m^{-2} at:
    - T = 800 ◦C
    - Applied cell voltage = 1.4 V
    - Electrical power density = 7 kW m^{-2}
    - w^e_{H2} = 37.5 kW h (kg H_2)$^{-1}$

⇒ superior to alkaline electrolyser performance

Specific electrical energy consumption:

$$w^e_{H_2} / \text{kW h (tonne H}_2)^{-1} = \frac{2F}{\Phi^e_{H_2}} \cdot \frac{U}{3.6 M_{H_2}}$$

However, this merely increases the amount of hydrogen produced by PV+SOE over that produced by PV + alkaline electrolyser by a factor of 1.73, giving 17 refuellings per year and hence 10,954 km of 6,808 miles = > still can't compete with electrical vehicles (i.e. Li-ion batteries)

BOC-Honda Hydrogen Refuelling Station, Swindon

- The station provides **refuelling capability at both 350 & 700 bar** and is capable of refilling 4 cars per hour.
- Max. H_2 mass requirement for 1 refill = 5.6 kg
- Take typical peak hours of station operation as ca. 7 am to 8 pm => 13 hours
- => Amount of hydrogen required ≈ 290 kg (H_2) day^{-1}.
- Hydrogenics www.hydrogenics.co.uk pressurised electrolysis modules specifically tailored for hydrogen refuelling of vehicles have specific electrical energy consumption:
  65 kWh (kg H_2)$^{-1}$ for 350 bar
  68 kWh (kg H_2)$^{-1}$ for 700 bar
- **Hence, for a single day's supply of hydrogen to a single commercial refuelling station need 290 × 68 = 19,720 kWh**

http://www.boconline.co.uk/en/processes/hydrogen-refuelling/index.html

Hydrogen Refuelling Station Case Study

BOC-Honda Hydrogen Refuelling Station, Swindon

290 kg (H_2) day^{-1} requires 19,720 kWh day^{-1}

Case Study: Conergy Solar Park (Hampshire, UK)

• 4.5 MW solar farm	• 24 acre site (97,124.6 m^2)
• 18,500 solar modules (fixed position)	• Polycrystalline silicon
• 243 W per module (peak output)	• Module arrays are 1.8 m apart
• ≈ £162 per module	• Module efficiency 15.3 %
• Module size [m]: 1.652×0.994×0.04 • Surface area: 1.64 m^2 (1.3 m^2 of ground space, assuming 37 ° panel inclination)	

In June:

- Solar irradiance ≈ 5.4 kWh m^{-2} day^{-1}

=> Extracted electrical energy ≈ 0.62 kWh m^{-2} day^{-1}

- Each module takes up ≈ 2.35 m^2 of ground space

⇒ **A commercial refuelling station requires ≈ 0.046 km^2, covered with ≈ 19,400 PV modules**

Is this feasible for every refuelling station?

Faraday's Law of Electrolysis

The current density is a direct measure of the specific reaction rate

$$O + \nu_e e^- \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftarrows}} R$$

Electron and material fluxes are coupled by a charge transfer reaction of oxidised (O – electron acceptor) and reduced (R – electron donor) components of redox couple (O|R) at electrode | electrolyte interface:

A = electrode area

F = Faraday constant = $N_{av} e^-$

I = current

j = current density = I / A

Specific reaction rate, *r*:

$$r \, / \, \text{mol m}^{-2} \text{ s}^{-1} = \frac{|I|}{\nu_e F A} = \frac{|j|}{\nu_e F}$$