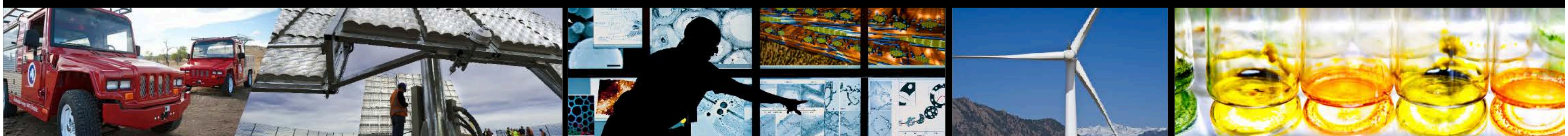
Practical Challenges in Scaling III-V Semiconductor-based Solar Hydrogen Systems



PECSYS (virtual) Workshop on Direct Production of Hydrogen from Sunlight

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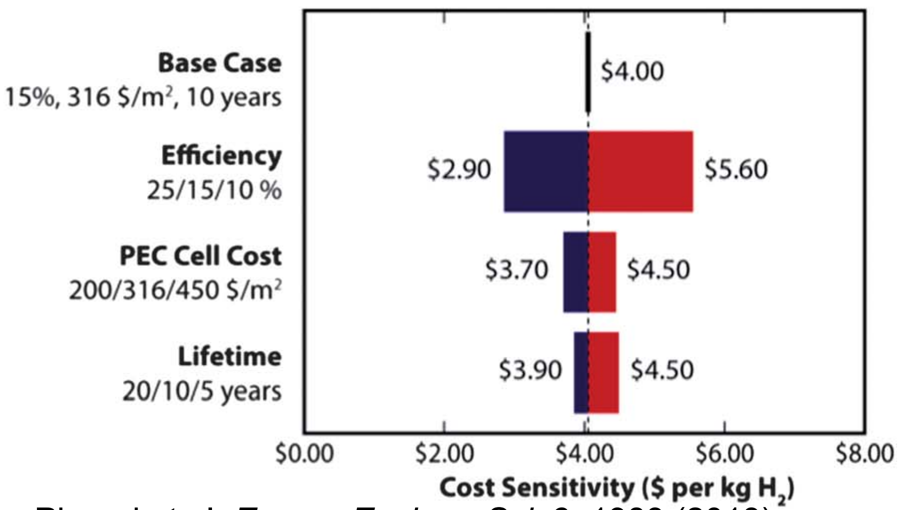
U.S. DOE long-term research targets

DOE EERE Multi-Year Research, Development, and Demonstration Plan

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Photoelectrochemical Hydrogen Cost [b]	\$/kg	NA	17.30	5.70	2.10
Capital cost of Concentrator & PEC Receiver (non-installed, no electrode) [c]	\$/m^2	NA	200	124	63
Annual Electrode Cost per TPD H_2 [d]	\$/yr-TPDH_2	NA	2.0M	255K	14K
Solar to Hydrogen (STH) Energy Conversion Ratio [e,f]	%	4 to 12%	15	20	25
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	3.3E-7	1.2E-6	1.6E-6	2.0E-6

Techno-economic analysis for a type 4 (10x concentrator) PEC reactor



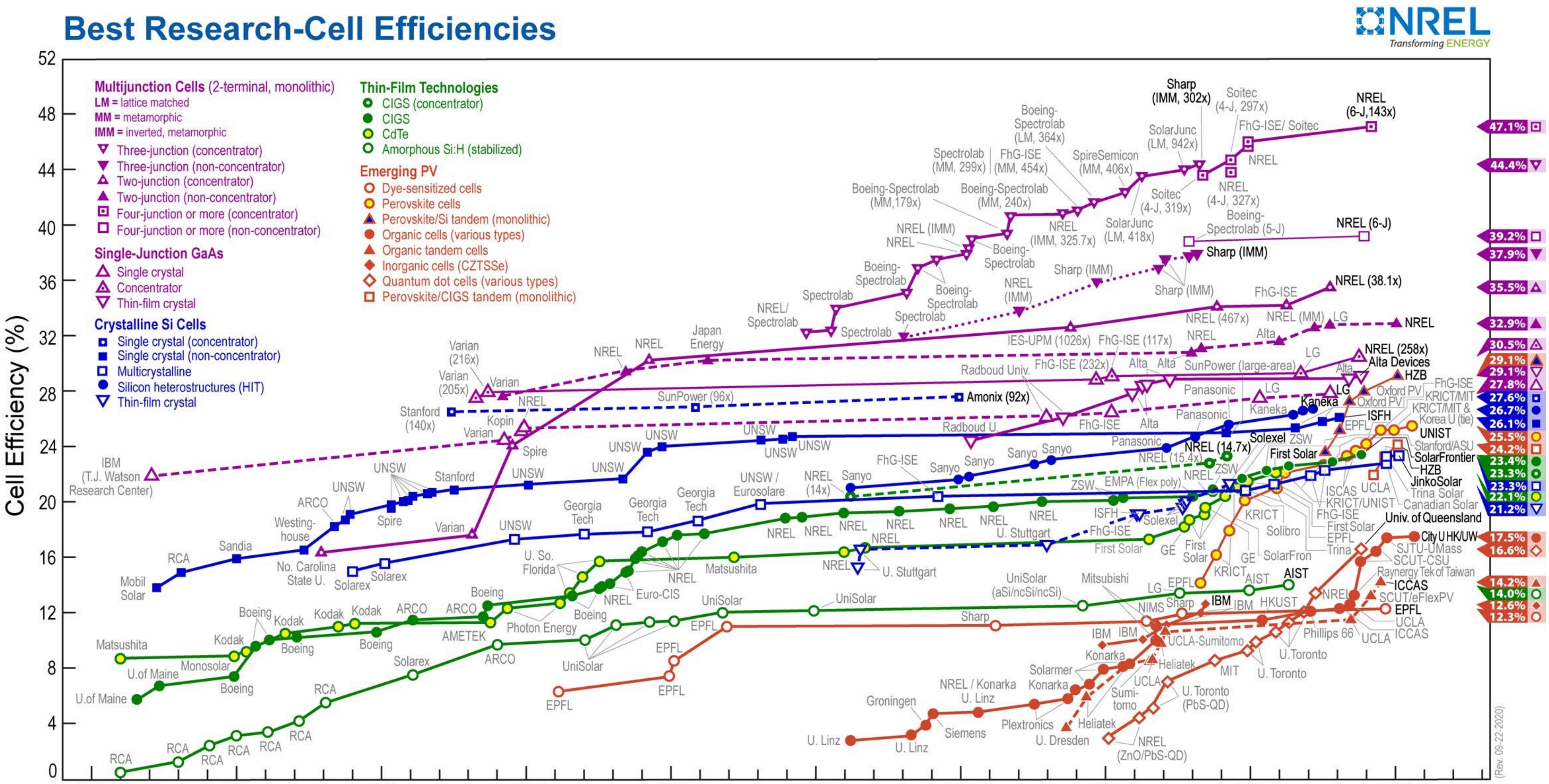
Pinaud et al. *Energy Environ. Sci.* **6**, 1983 (2013)

- Solar-to-hydrogen efficiency is the largest lever to reduce H_2 costs according to techno-economic analysis*

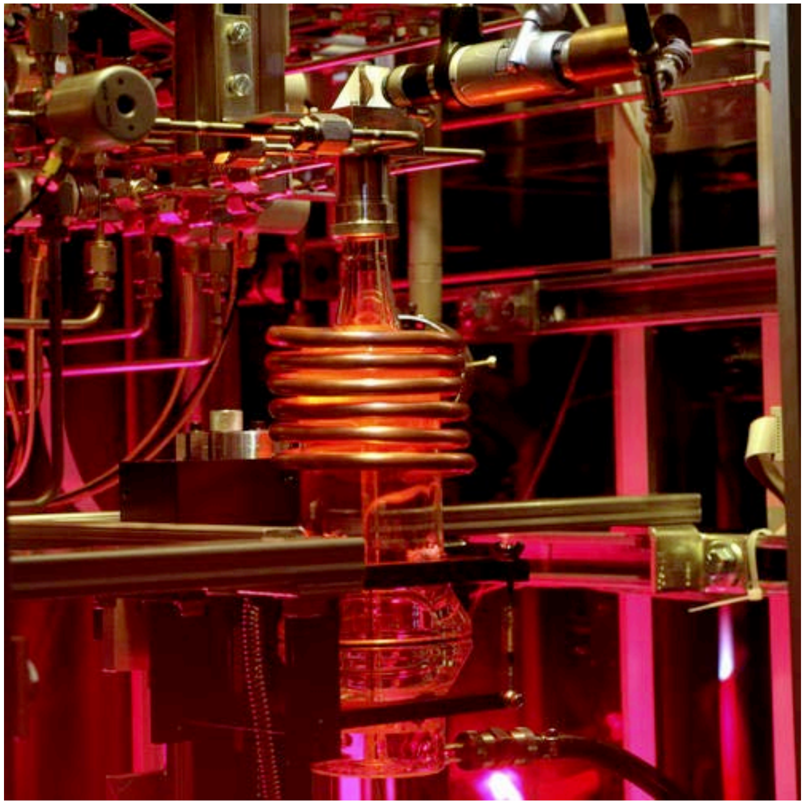
*within the optimistic cost and lifetime values modeled

Best research photovoltaic cell efficiencies

Look to PV efficiencies for PEC materials

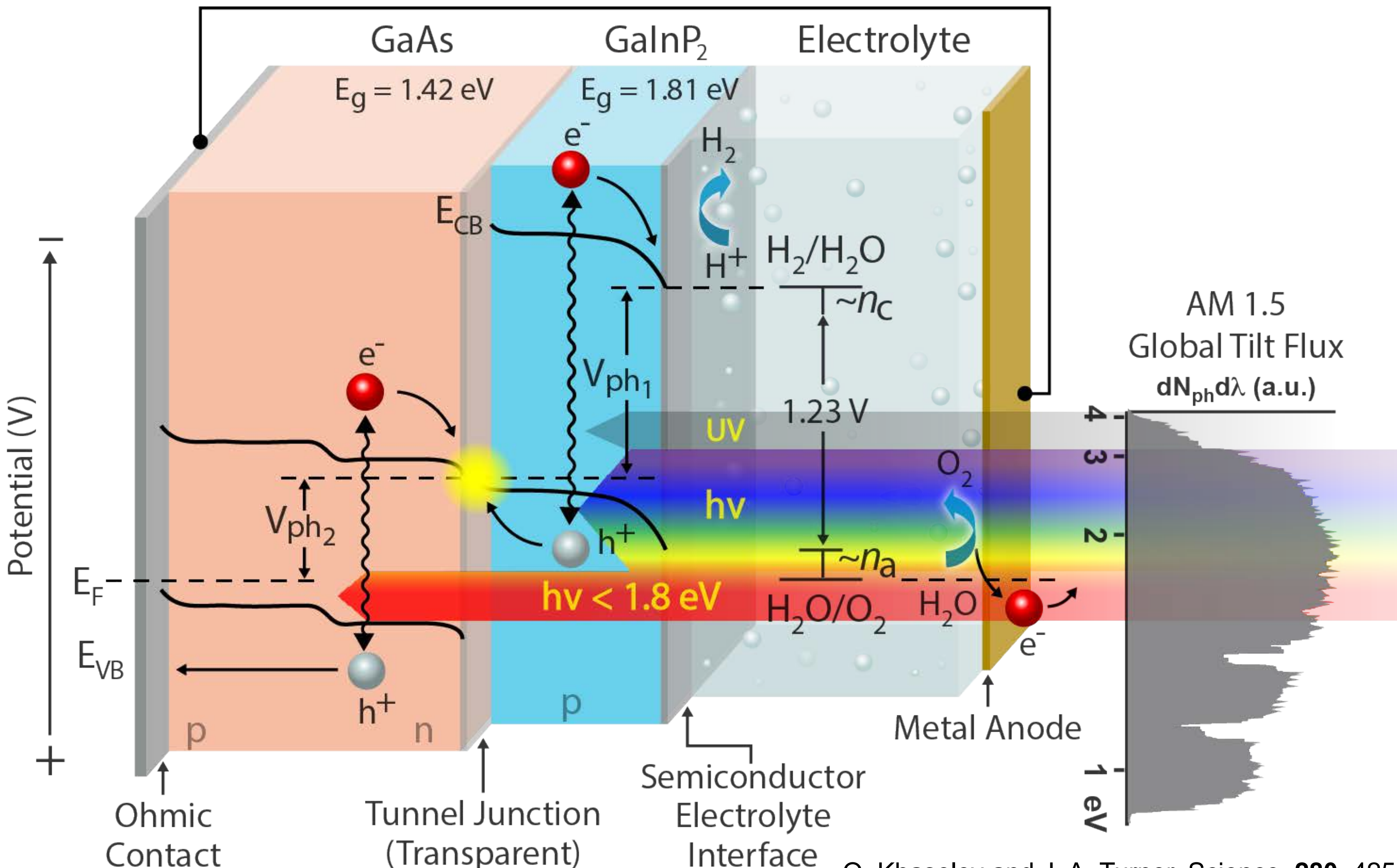


III-V synthesis



- **Metal organic chemical vapor deposition (MOCVD)**
  - NREL's III-V group
  - Atmospheric pressure in hydrogen carrier gas (6 SLPM!!!)
  - Triethylgallium, Arsine, Trimethylindium, Phosphine, Dimethylhydrazine
  - 700°C heated p-GaAs substrate (\$10,000/m^2)
  - Single-crystal epilayer films 4-5 μm thick

Stacked tandem spectral splitting

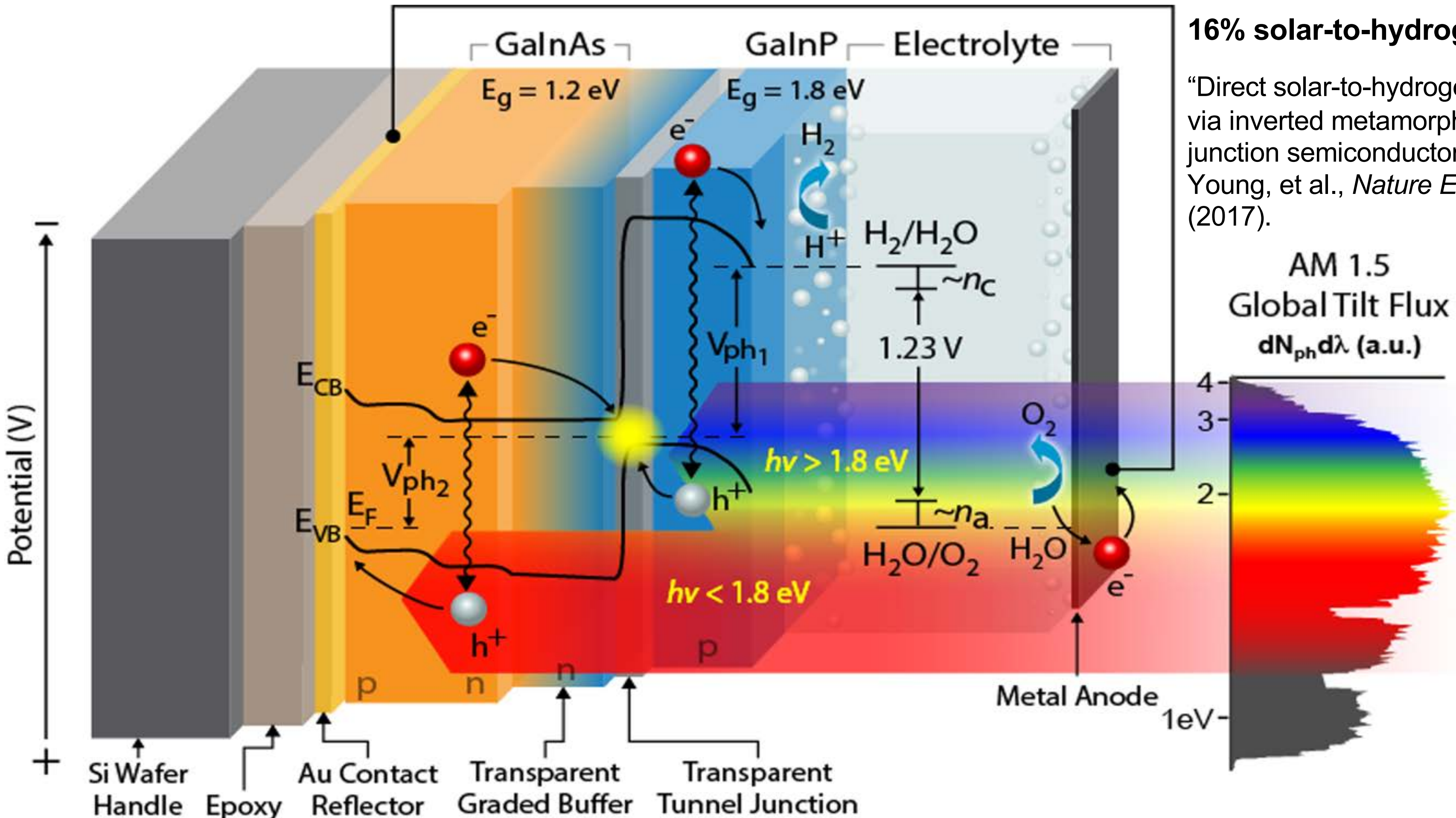


O. Khaselev and J. A. Turner, Science, **280**, 425 (1998).

Absorbers are connected electrically in series

– Voltages add, currents equal (current matching)

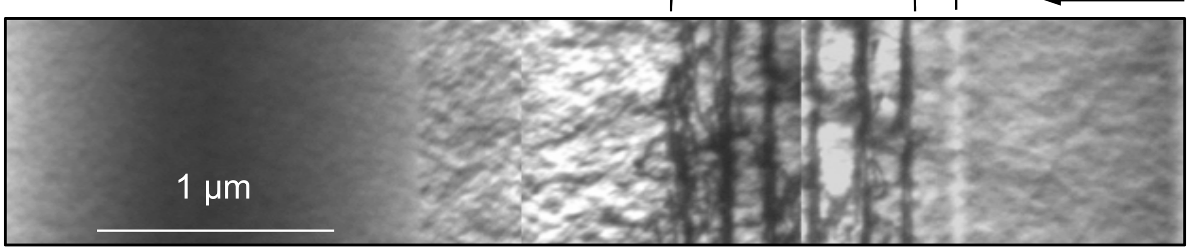
IMM spectral splitting



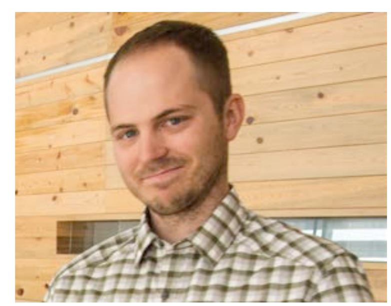
16% solar-to-hydrogen efficiency

"Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures" Young, et al., *Nature Energy* **2**, 17028 (2017).

growth direction

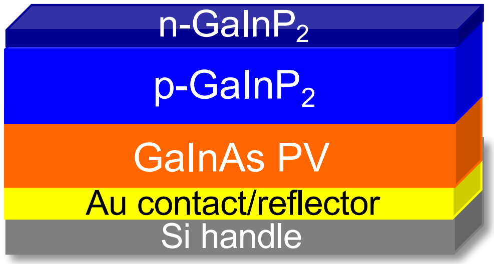


TEM cross-section



James Young

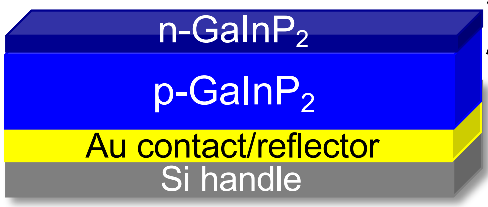
Buried junction to improve Voc



IMM-pn

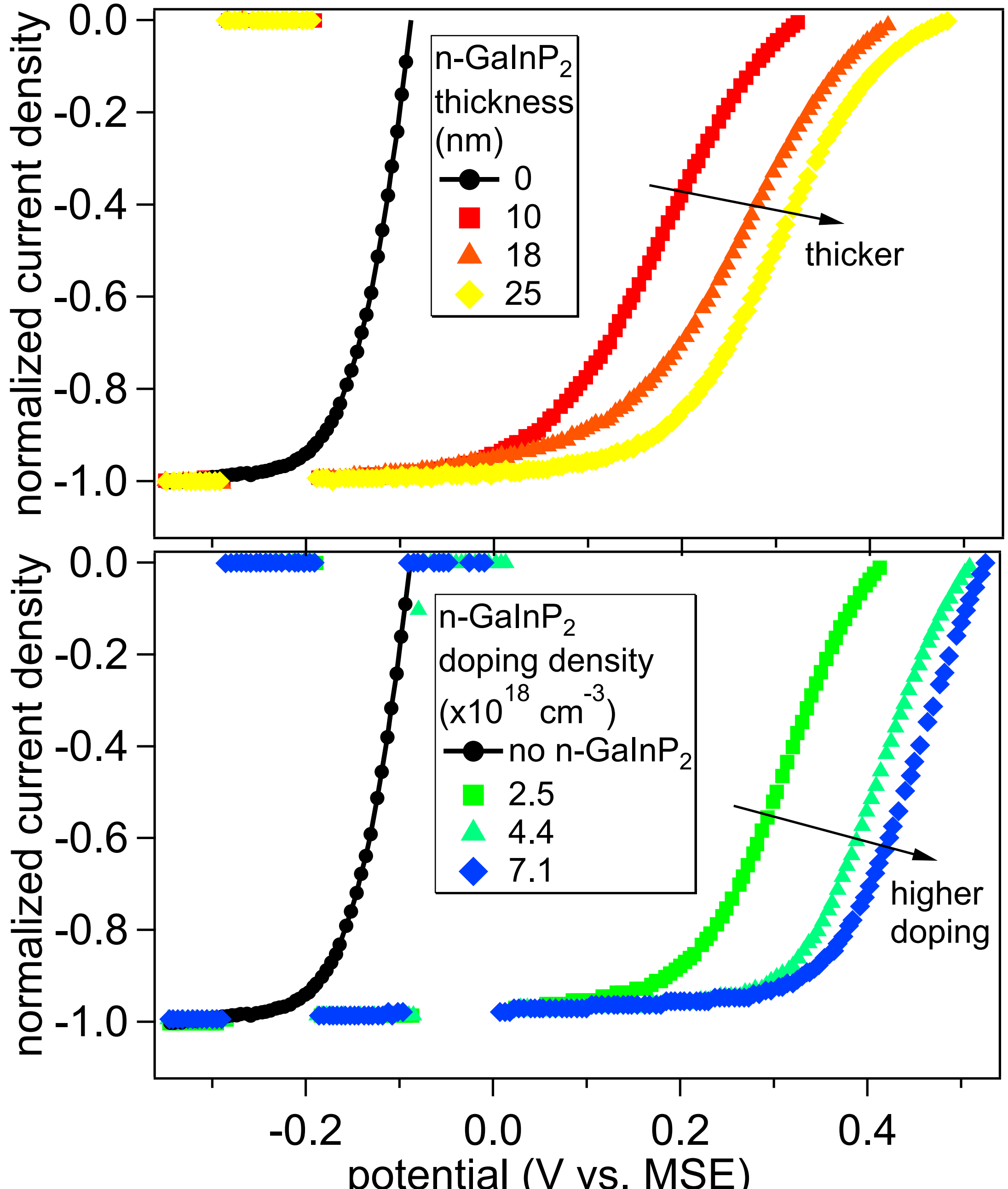
1) vary n-$GaInP_2$ thickness

(top junction only)

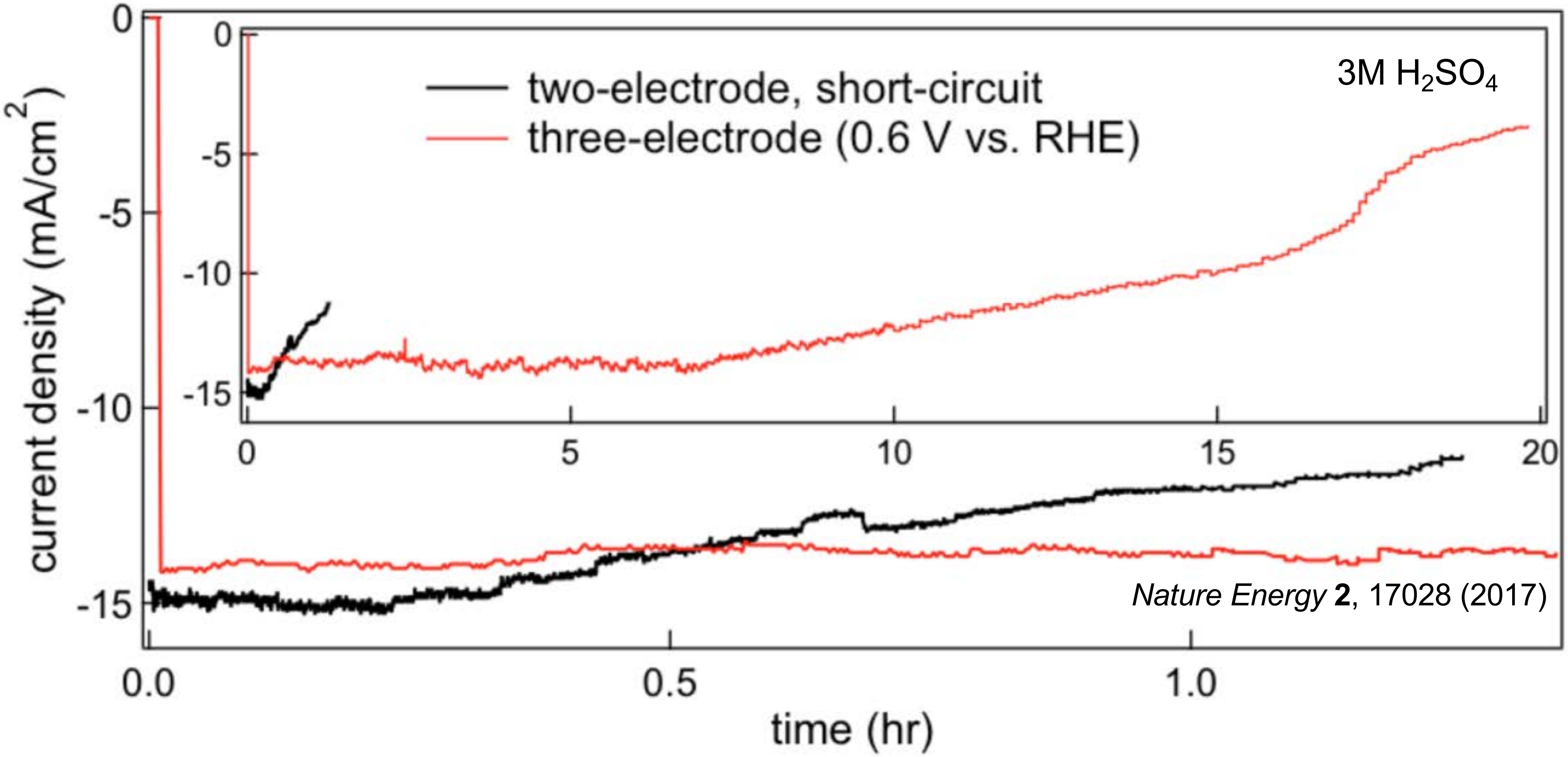


2) vary n-$GaInP_2$ doping

$GaInP_2$-pn test structure for optimizing photovoltage



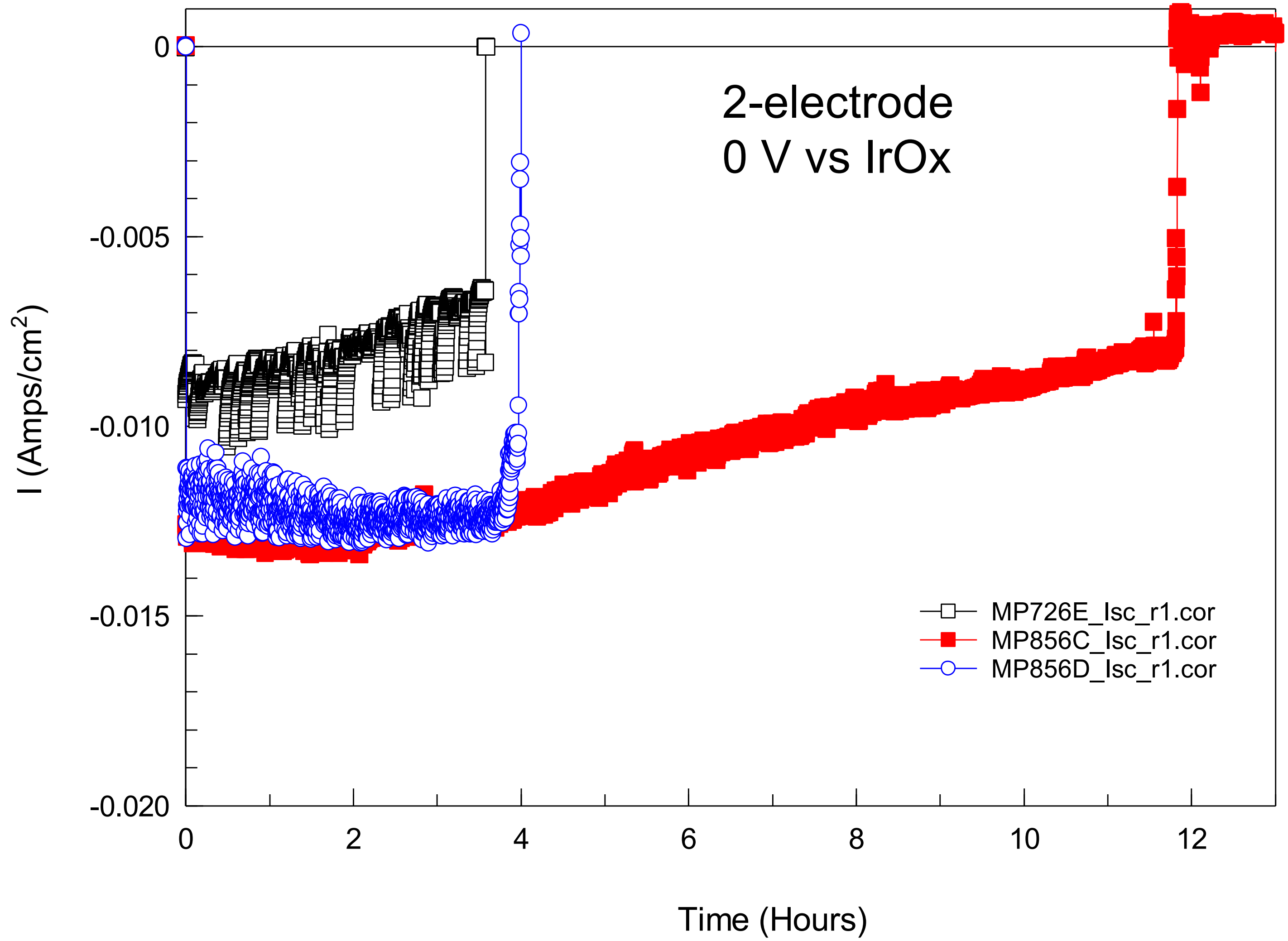
Insufficient durability



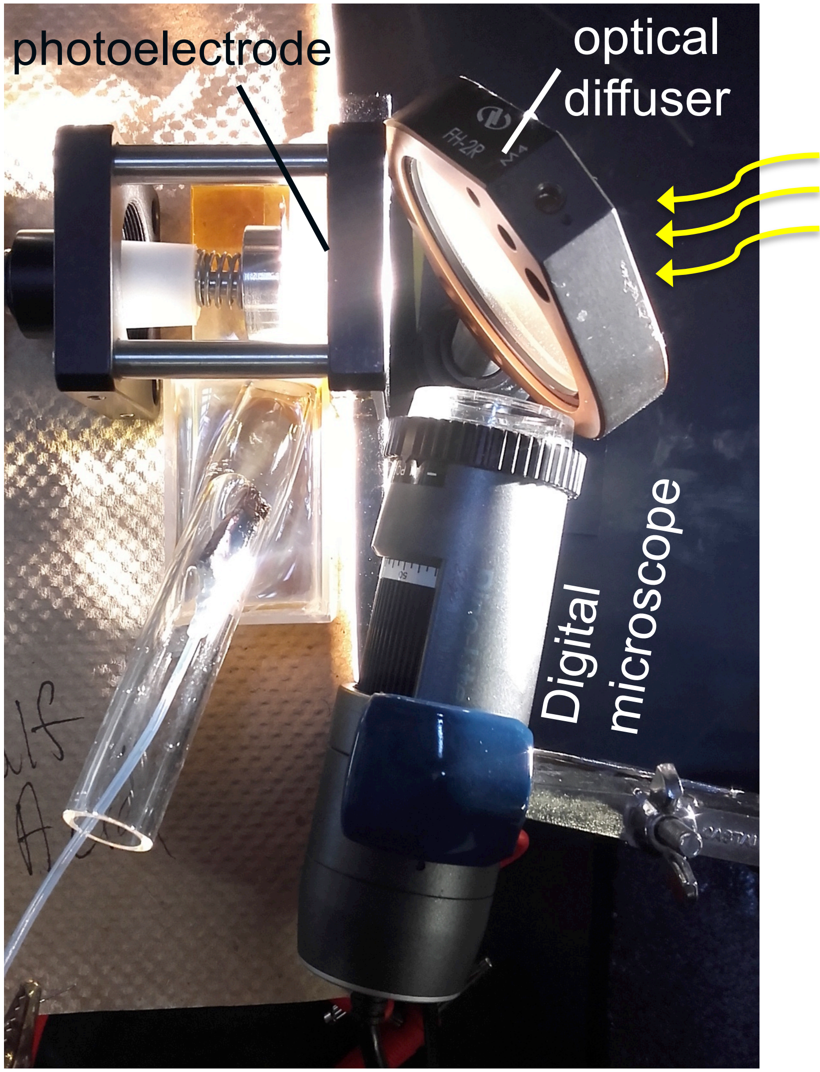
- III-V stability is a major problem
- Inverted metamorphic form-factor has additional degradation pathways
- Surface modifications to impart stability are inadequate
  - Nitridation-sputtering of PtRu; Atomic layer deposition (ALD) of protective film; Protective and catalytic application of 2D materials – molybdenum disulfide (MoS_2); Engineered epitaxial capping layer
- Several days to grow and process each III-V sample
  - ~$50,000/m^2 – replacing after a couple hours is not feasible

Best durability so far

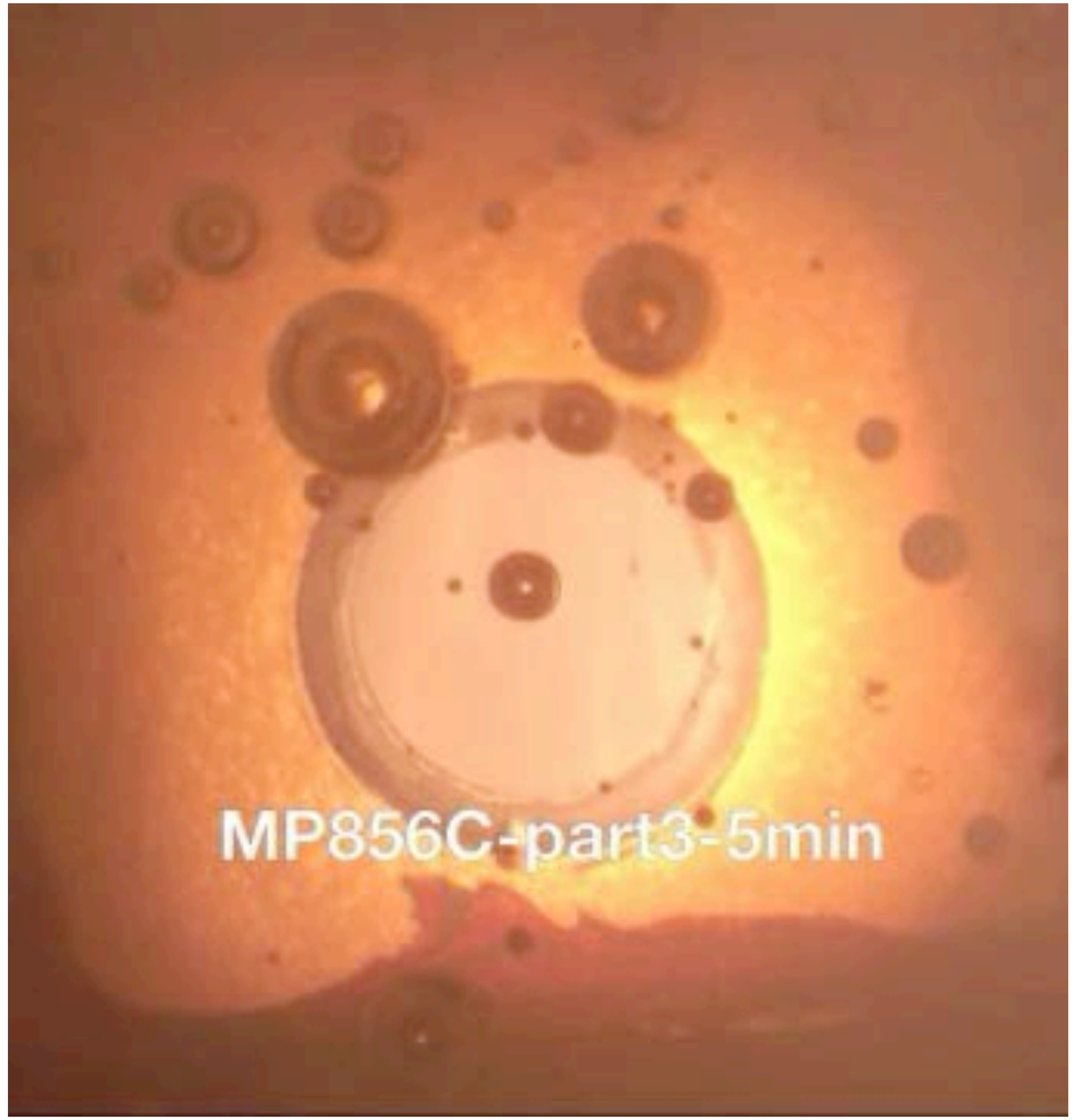
- **GaInAsP (1.7eV) lattice matched on GaAs (1.4eV) – inverted but not metamorphic**
- **MoS_2 applied by Jaramillo group (Stanford)**
- **Short-circuit testing in 0.5M H_2SO_4**
- **Failed at 12 hours, corrosion initiating at pinhole defect.**



Evolution: Defect to destruction



Mirror image: observing reflection

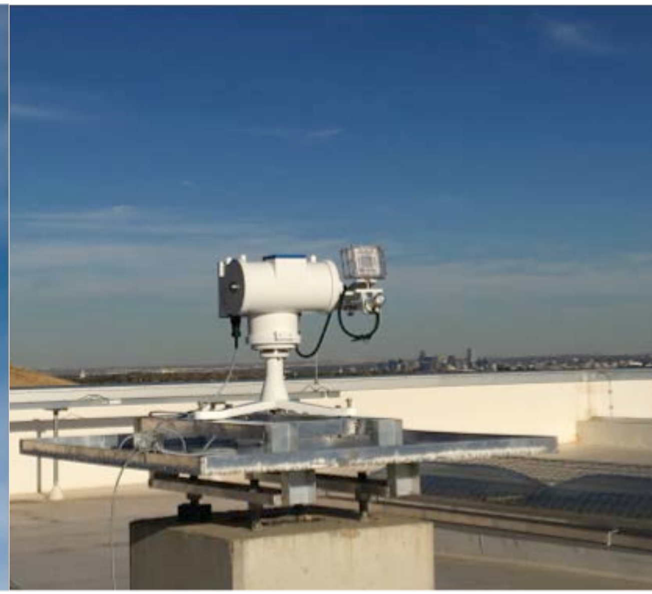


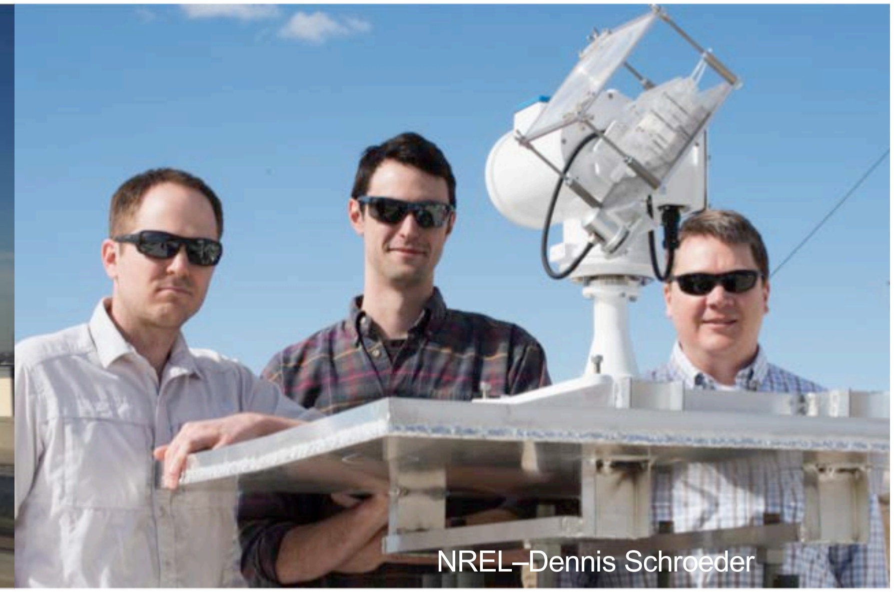
Approximately hours 8-10, 5-minute photo intervals

Photoreactor testing

Photoreactor demonstration

Incorporate most efficient and stable material in a photoreactor on a tracker and demonstrate 8 hours of continuous operation in sunlight with a cumulative production of at least 3 standard liters of H_2 (Sept 2017)





- To get 3 standard liters of H_2 in 8 hours need
  - 8 cm^2 of IMM absorbers @ 15% STH efficiency, 100 % Faradaic efficiency
    - Two or three photoreactors on solar tracker
  - 10x optical concentration (lens cost $4400/$m^2$)
  - Reasonable durability
  - Sunlight

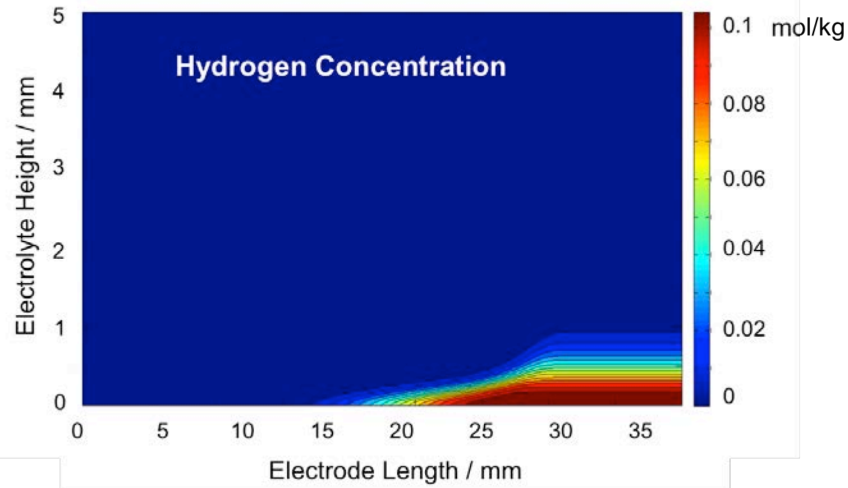
J (mA/cm^2)	Area (cm^2)	Time (min)	Temp(K)	Pressure(atm)	Moles H2	Volume(ml) H2
125	8	480	273	1	0.149	3343

Multi-physics modeling of 10x concentrator cells and prototype fabrication for on-sun measurements

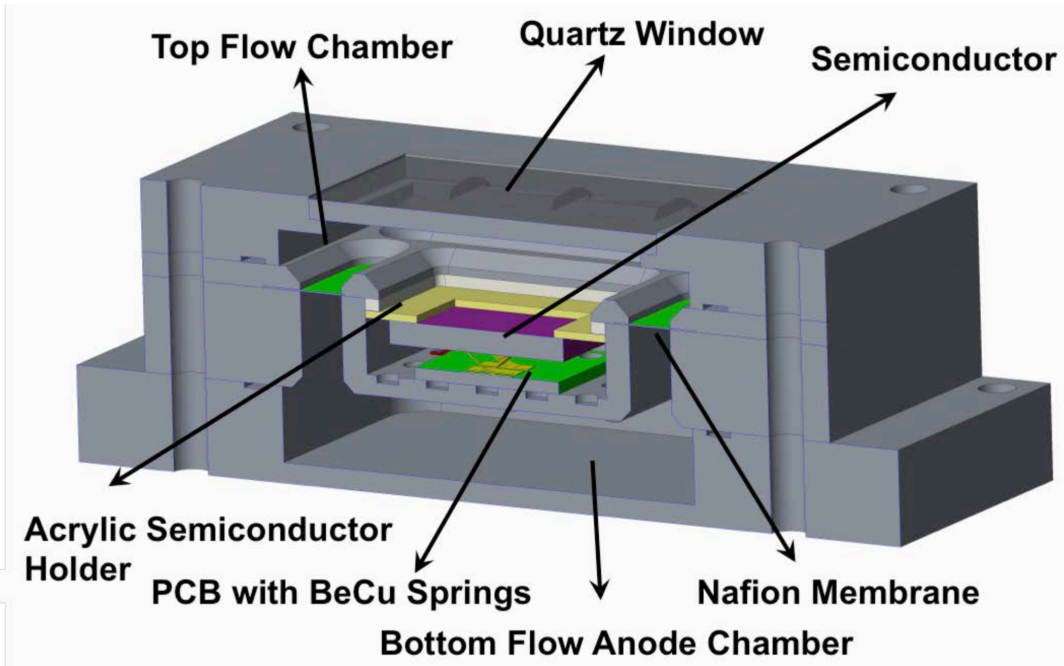
Modeling of PEC reactor shows 10x concentration is feasible; pressurization to inhibit bubbles is not

COMSOL on NREL's supercomputer (Anthony Abel)

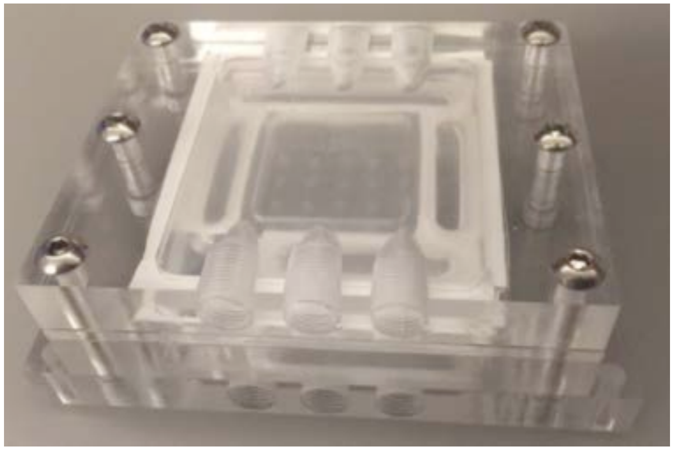
- Laminar flow in PEC chamber
- H_2 concentration
- Optical path through electrolyte
  - ≤5 mm electrolyte thickness
- H^+ / HSO_4^- distribution
  - Potential drop through electrolyte ~300 mV
- Overvoltage
  - ~80 mV (HER) + ~220 mV (OER) + 300 mV (solution)
  - Total voltage necessary = ~1.85 V



Only first 30 mm include generation: flow left→right 30 mm/s (avg)
Minimum pressure to keep hydrogen in solution : **147 atm**



Using pressure to keep H_2 from bubbling and scattering light is not feasible under these conditions



Prototype chassis machined from PMMA
Concentration via Fresnel lens mounted to reactor

Photoreactor: H_2 production context

3 standard liters of H_2

$$3\ l\ H_2 * \frac{mol\ H_2}{22.4\ l\ H_2} * \frac{2\ mol\ e-}{mol\ H_2} * \frac{96485\ C}{mol\ e-} * \frac{Ah}{3600\ C} = 7.18\ Ah$$

Would propel a fuel cell vehicle how far?

$$3\ l\ H_2 * \frac{mol\ H_2}{22.4\ l\ H_2} * \frac{0.002\ kg\ H_2}{mol\ H_2} * \frac{70\ miles}{kg\ H_2} * \frac{5280\ ft}{mile} = 99\ ft = 30\ m$$

Context

- **How large an area for a 10% STH system (~8 mA/cm²) to generate 1kg H_2 in an 8-hour day?**

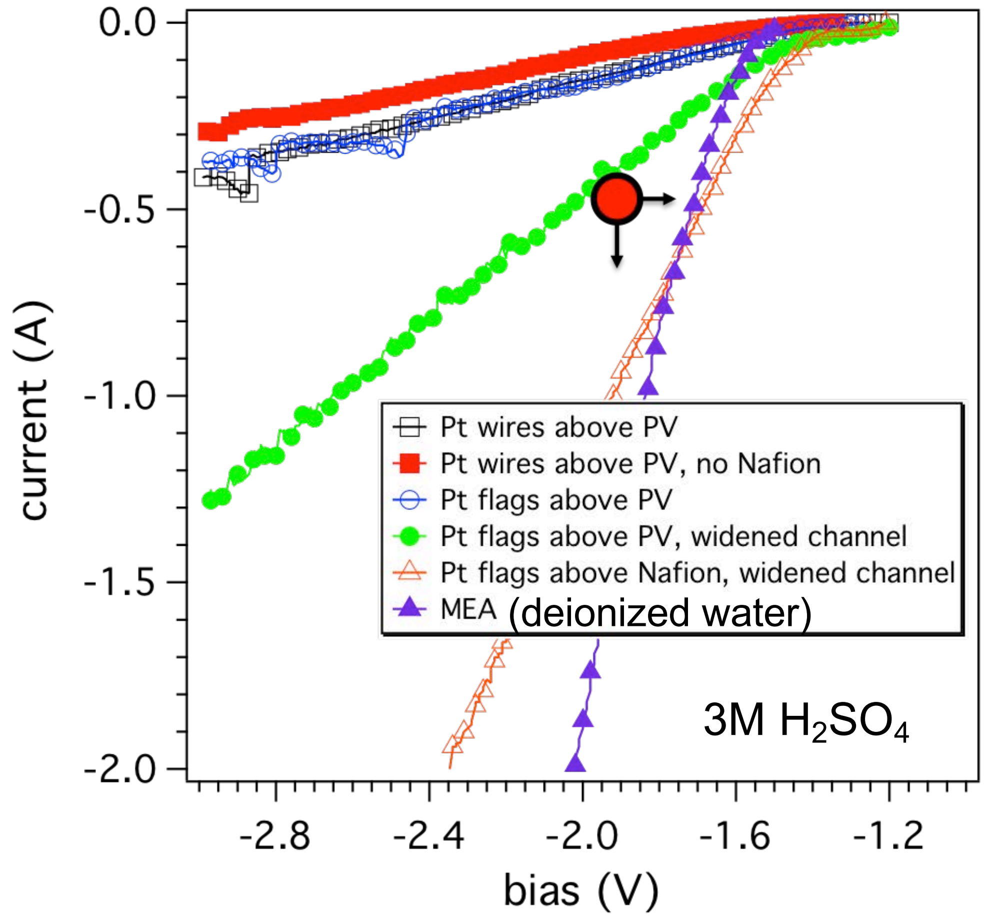
$$\frac{8\ mC}{s \cdot cm^2} * \frac{1\ C}{1000\ mC} * \frac{3600\ s}{h} * \frac{1\ mol\ e-}{96485\ C} * \frac{1\ mol\ H_2}{2\ mol\ e-} * \frac{0.002\ kg\ H_2}{1\ mol\ H_2} * \frac{10{,}000\ cm^2}{m^2} = 0.00302\ \frac{kg\ H_2}{m^2 \cdot h}$$

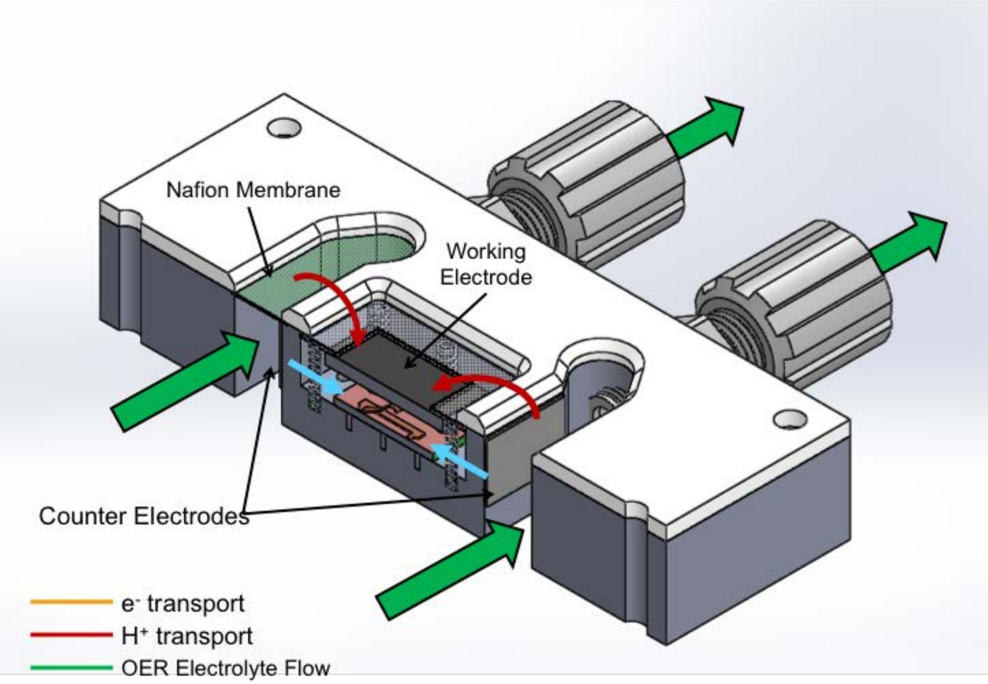
$$0.00302\ \frac{kg\ H_2}{m^2 \cdot h} * 8\ h = 0.0242\ \frac{kg\ H_2}{m^2}$$

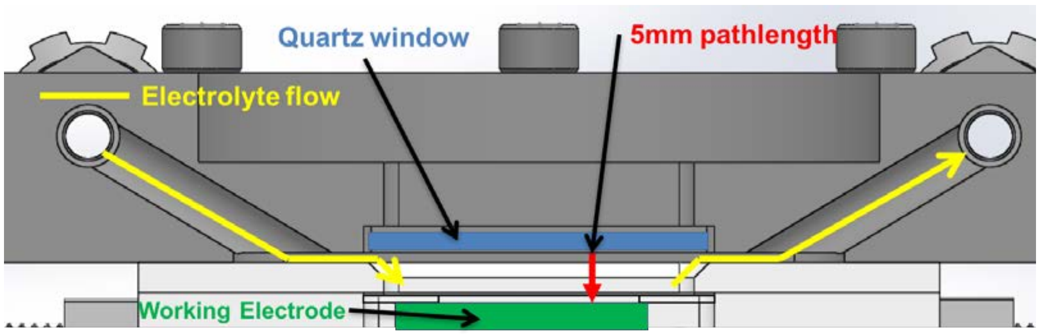
$$41.3\ \frac{m^2}{kg\ H_2}$$

Integrated (encapsulated) PV electrolysis

- **Design electrolysis components that target >500 mA at 2 V**
  - Cathode size not an issue
  - Widening channel improved performance
  - Cathode placement is critical, even in 3M H_2SO_4

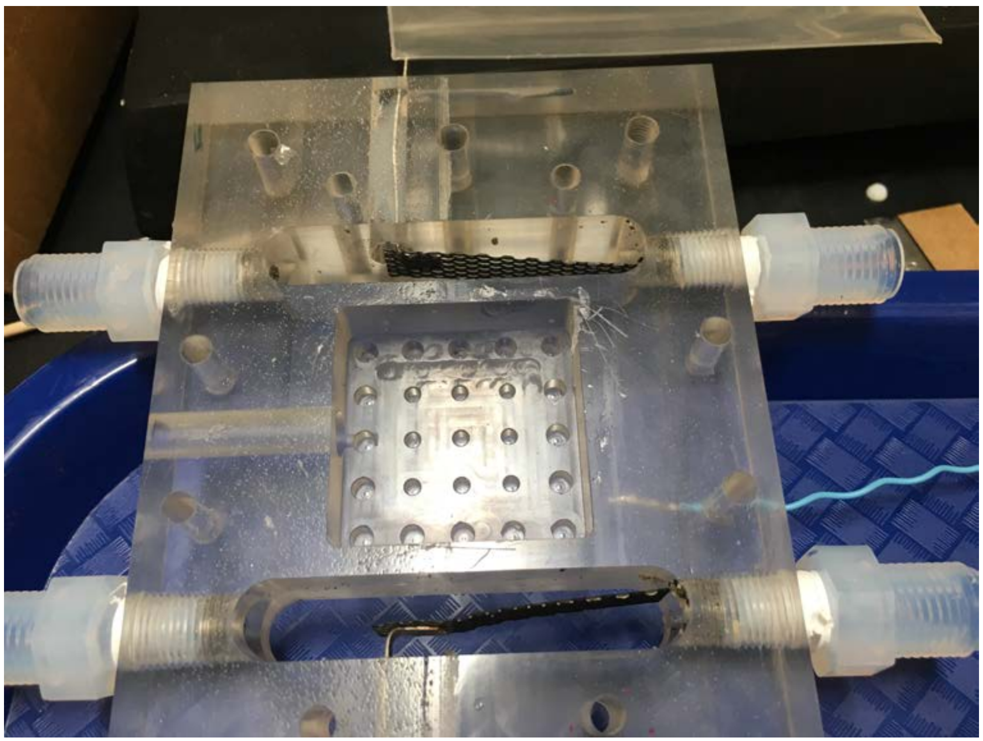






Anode issues

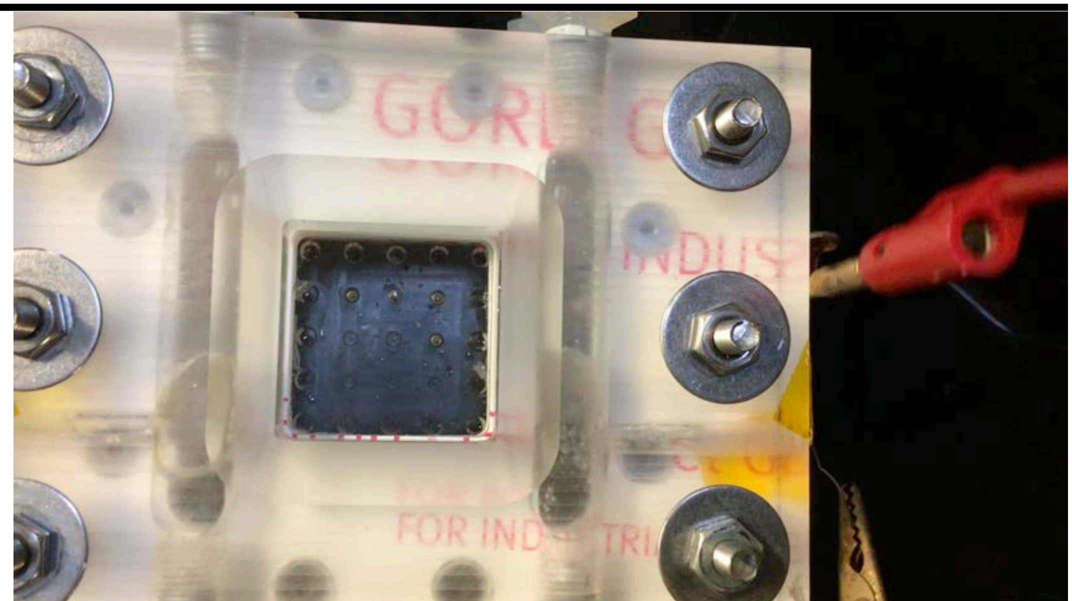
- **Oxygen evolution from water oxidation in 3M H_2SO_4**
  - RuOx anodes are highly active, but unstable in acid
  - IrO_2 based catalyst coated on Ti mesh
    - Provided by Water Star Inc.

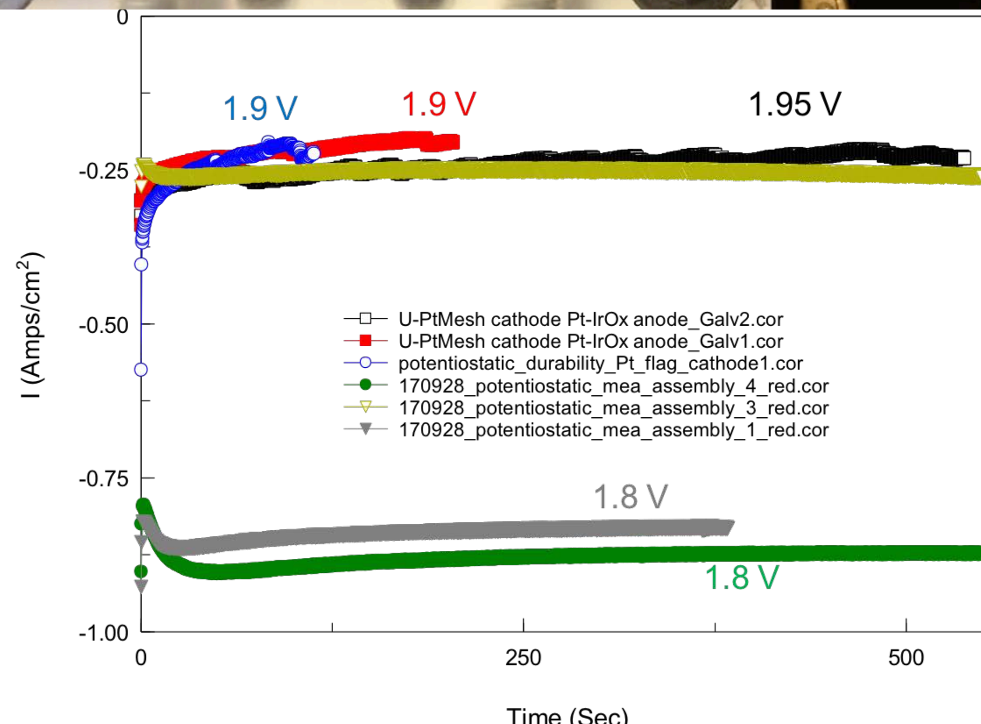


Cathode issues

- **Hydrogen evolution from proton reduction in 3M H_2SO_4**
  - H_2 bubbles stuck to cathode
  - Pumping, channel redesign
  - Pt flags, Pt black, Pt mesh

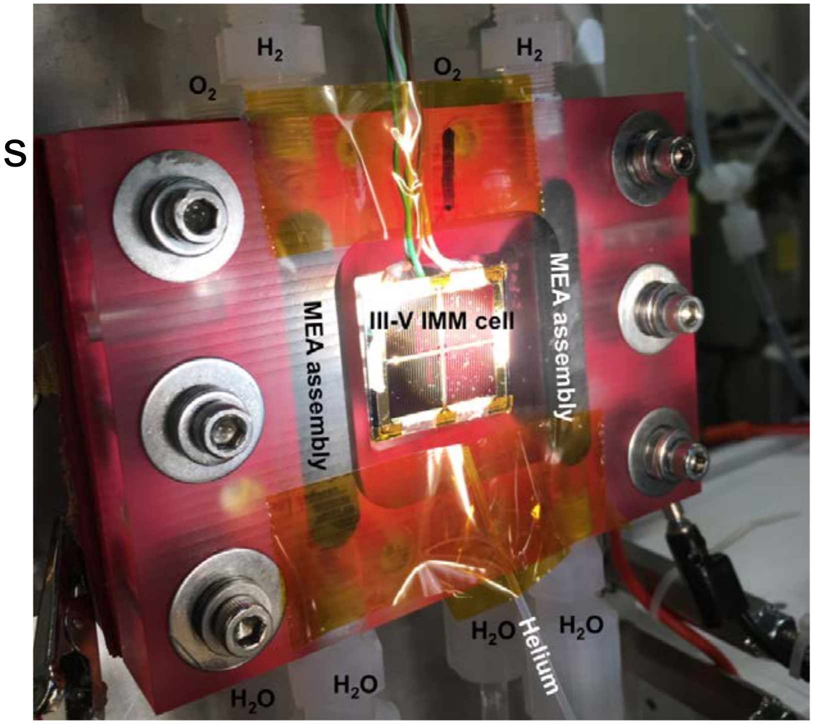
~~Pressure~~, ~~surfactant~~

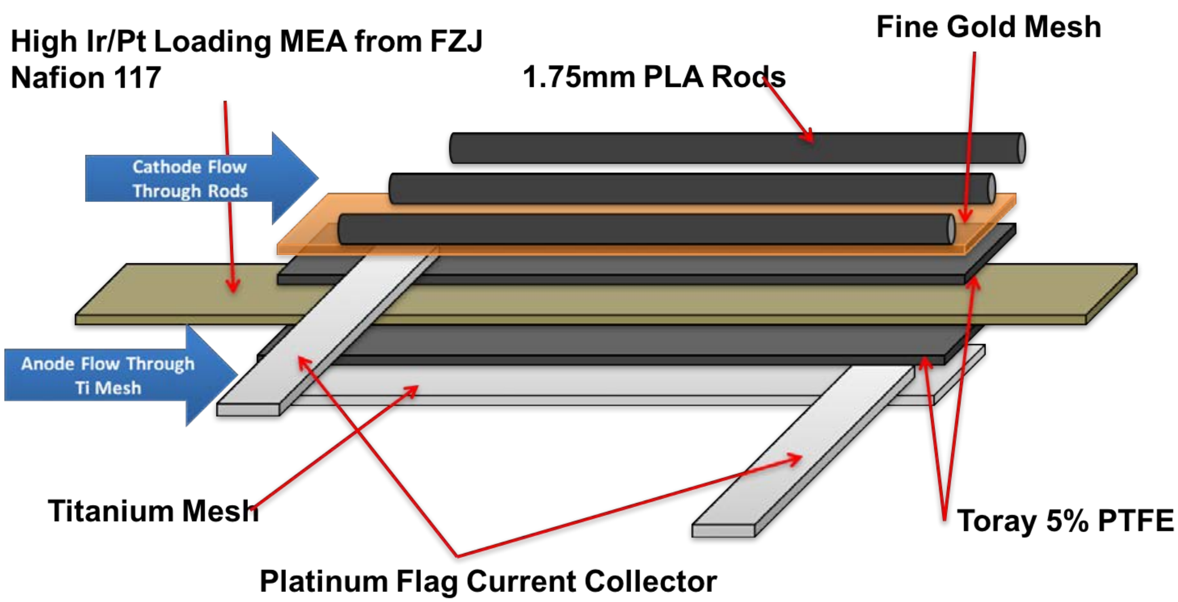


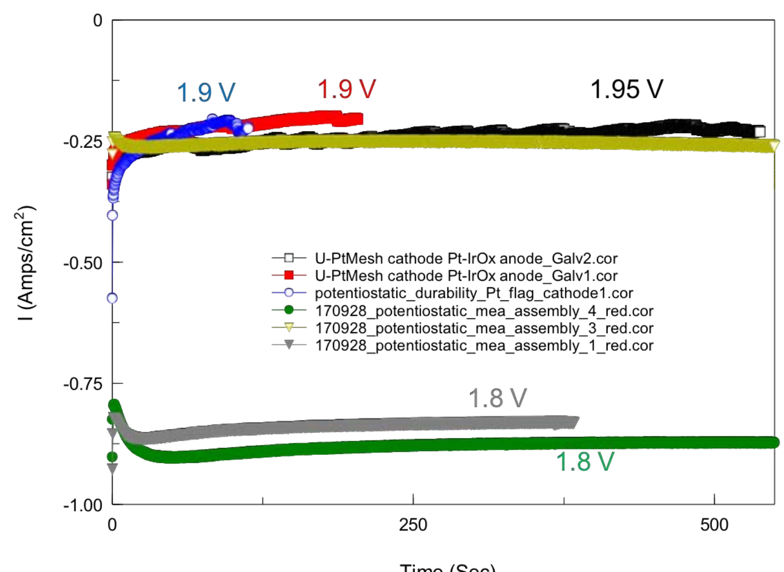


Integrated PV/PEM electrolysis

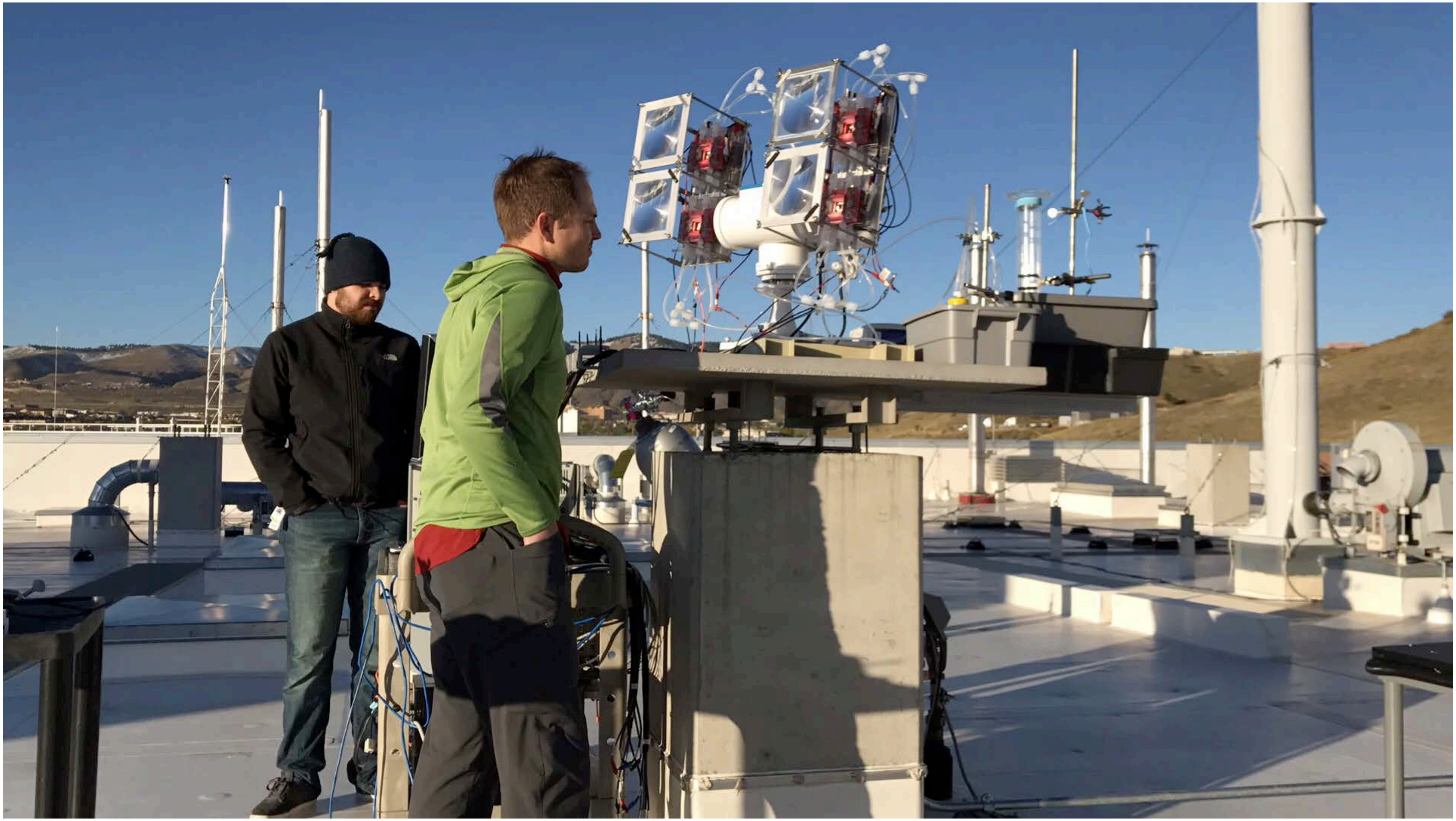
- **Only solution to bubbles was to use membrane electrode assemblies (MEA)**
    - High water splitting current densities at low bias
    - Stable output (no bubble issues)
    - Deionized water is the reactant
- **Fully processed PV**
    - Window layer, contact layer, metal contacts, AR-coating, **helium cooled**
    - 1.8 eV $GaInP_2$ on 1.2 eV InGaAs
    - Four arrays, each with four 1 cm x 1 cm cells



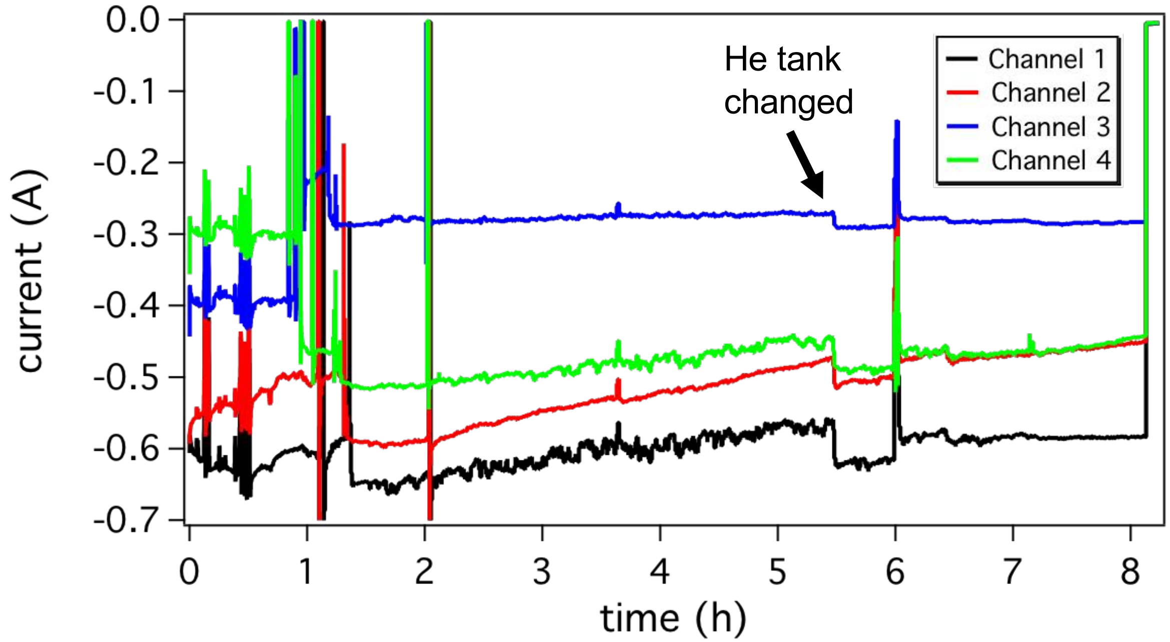


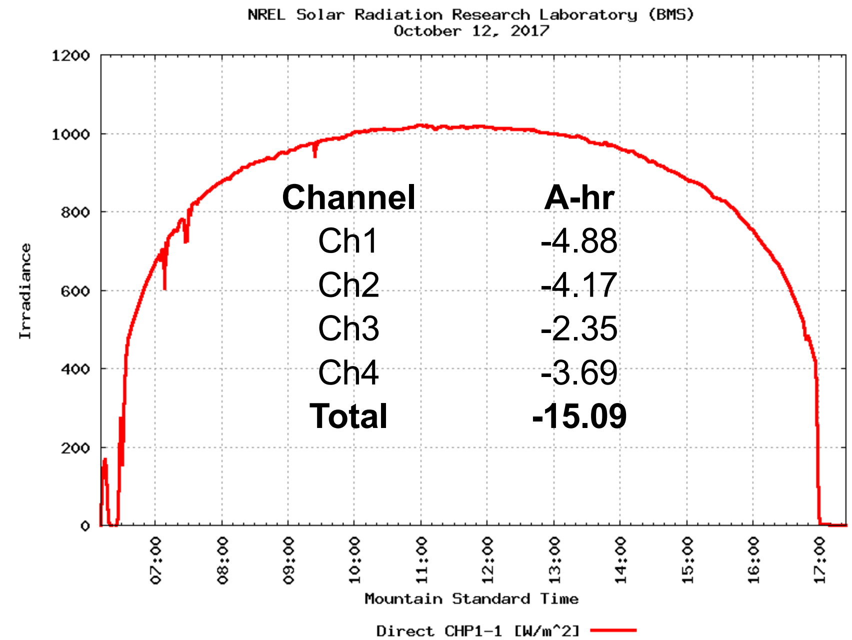


Time-lapse outdoor run

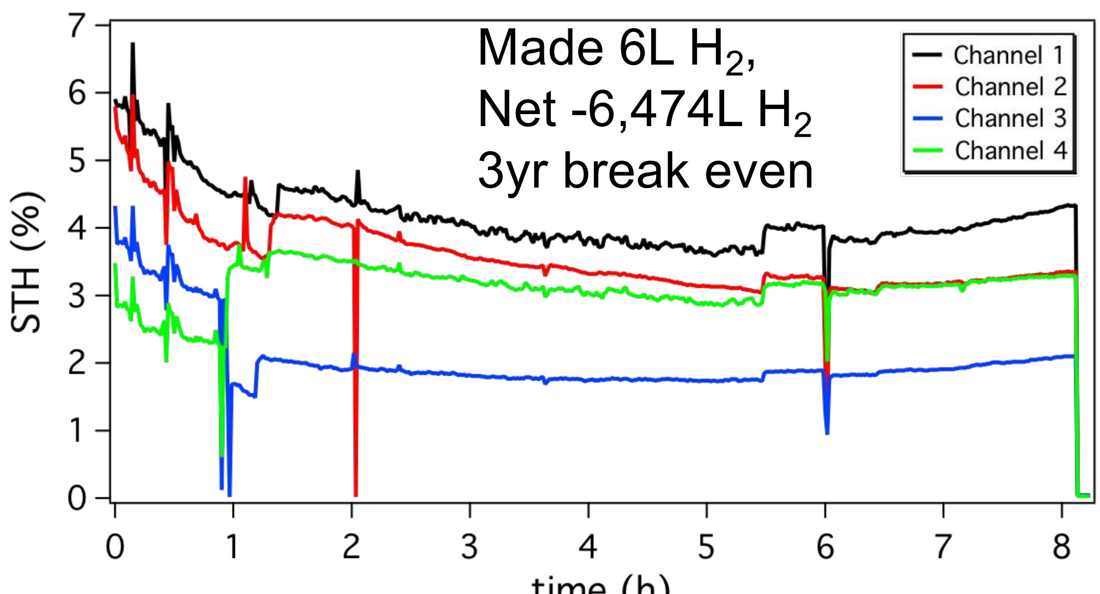


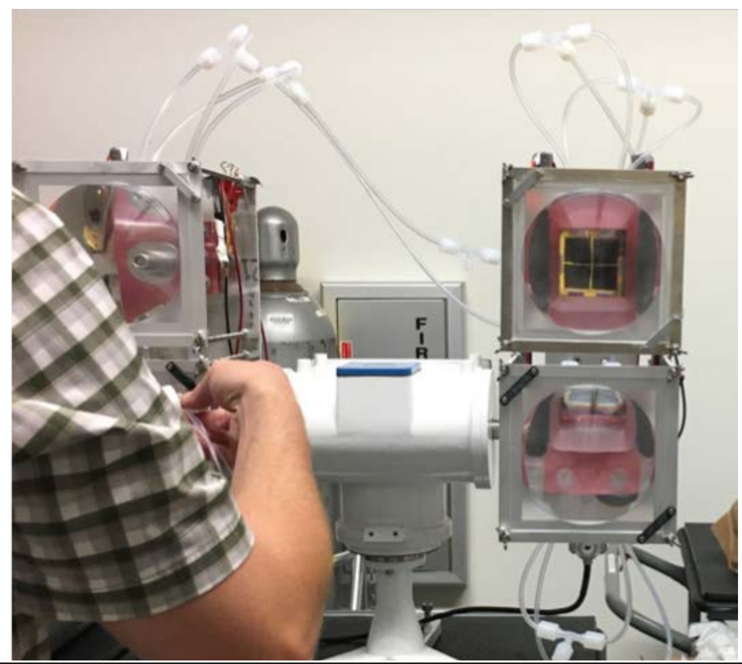
Outdoor performance





Channel	**A-hr**
Ch1	-4.88
Ch2	-4.17
Ch3	-2.35
Ch4	-3.69
Total	**-15.09**





Summary

- **III-V inverted metamorphic multijunctions**
  - Increased efficiency
  - Durability is compromised
  - Cost is prohibitive
- **Photoreactor scale up**
  - PEC instability prevents scale up of III-Vs
  - Practical challenges
    - Ionic transport, bubbles, thermal management
  - Still a long way from significant scale

Acknowledgements

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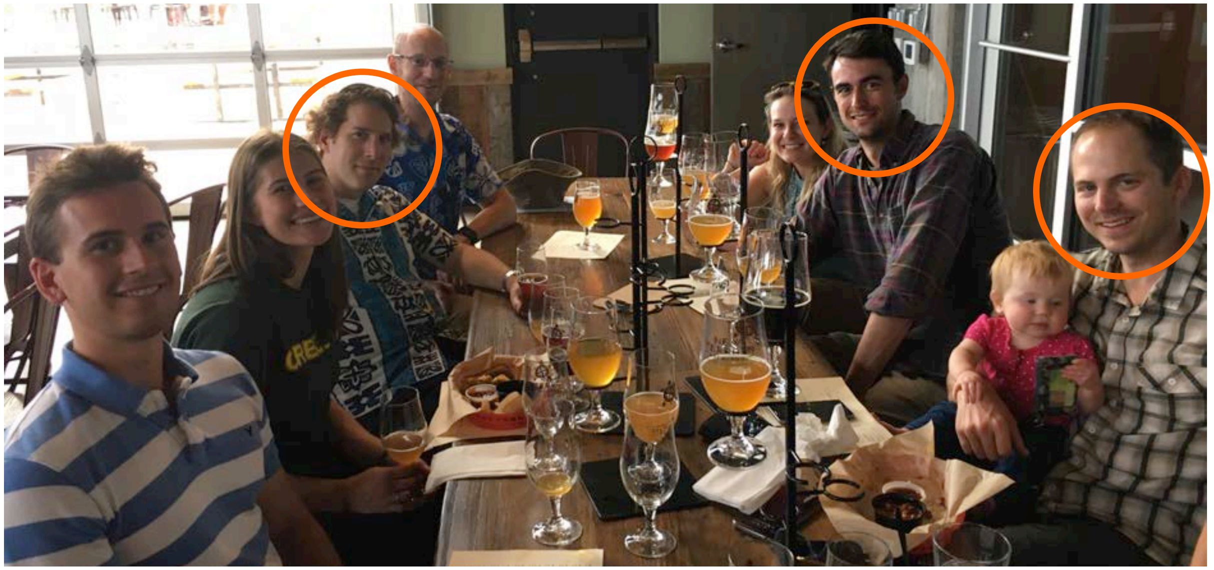
- **Project Partners**
  - NREL
    - PEC: John Turner, James Young, Henning Döscher
    - III-V synthesis: Myles Steiner, Dan Friedman, John Geisz, Ryan France, Waldo Olavarria
    - Photoreactor: Ellis Klein
- **Collaborators**
  - Stanford
    - Tom Jaramillo, Reuben Britto



NREL–Dennis Schroeder

Thank You