Ultra-Light Weight PEC…
and Chemistry/Purity Information

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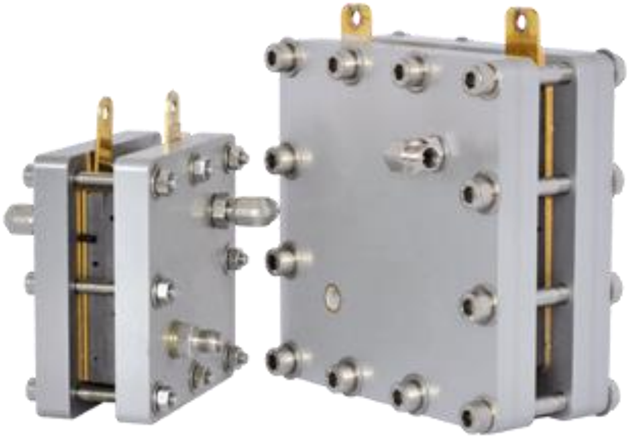
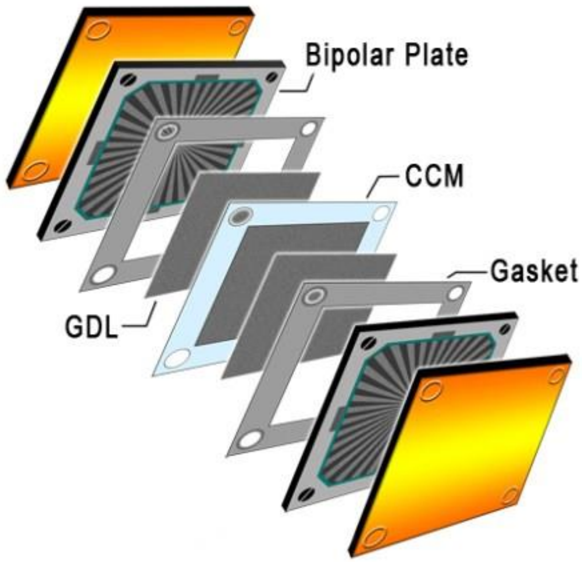
ULW PEC Device/System

- Design
  - Photon Management
- Deployment
- Metrics (W/kg, kg/m^2)
- System Scaling
- Filter (chemical inputs/outputs)





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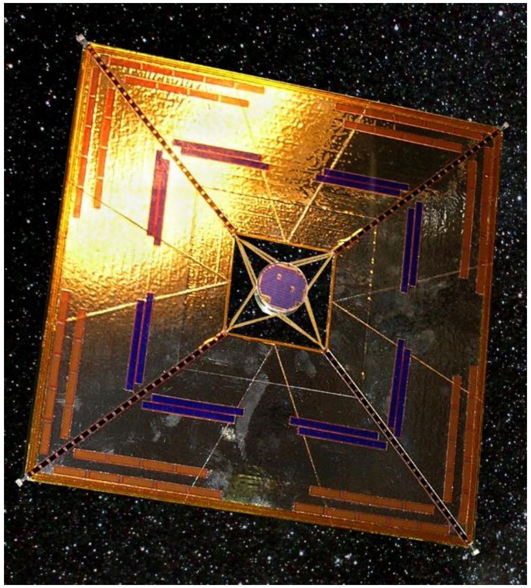
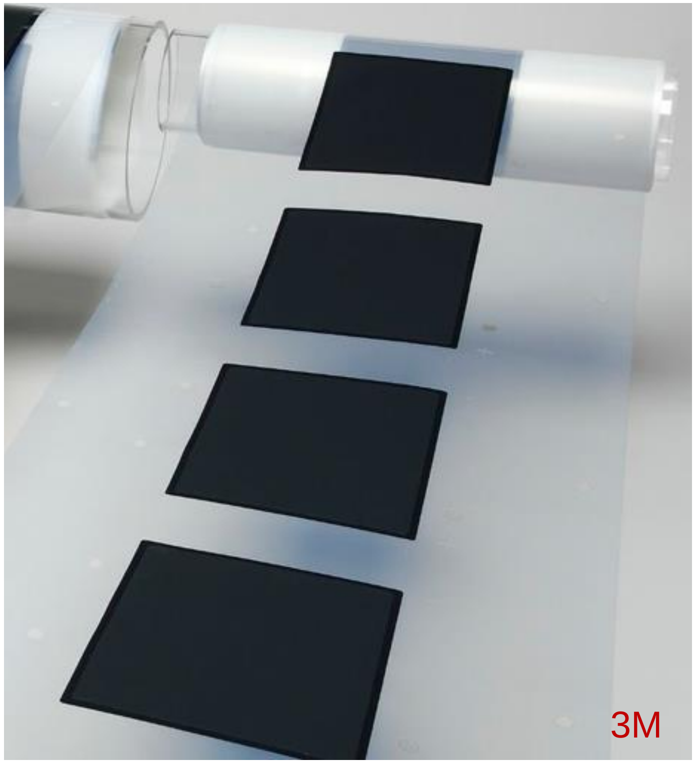
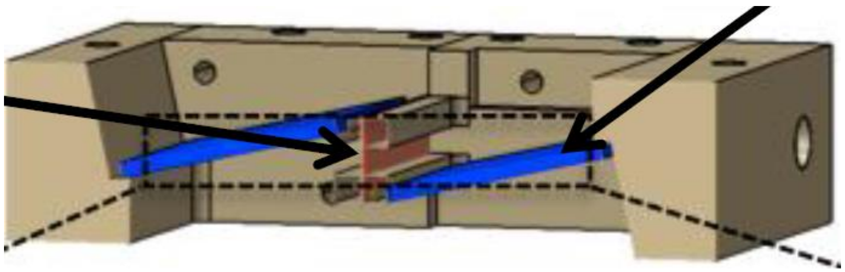


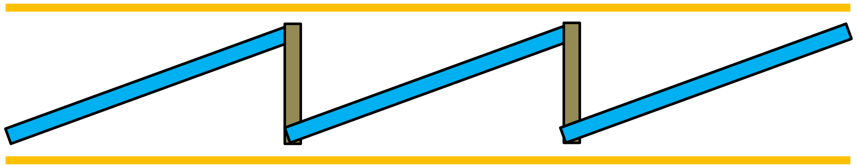


ULW PEC Considerations

- Transport dry/empty and fill on Mars
- Roll out material
- Autonomously
  - Adopts flat geometry
  - Creates volume for electrolyte

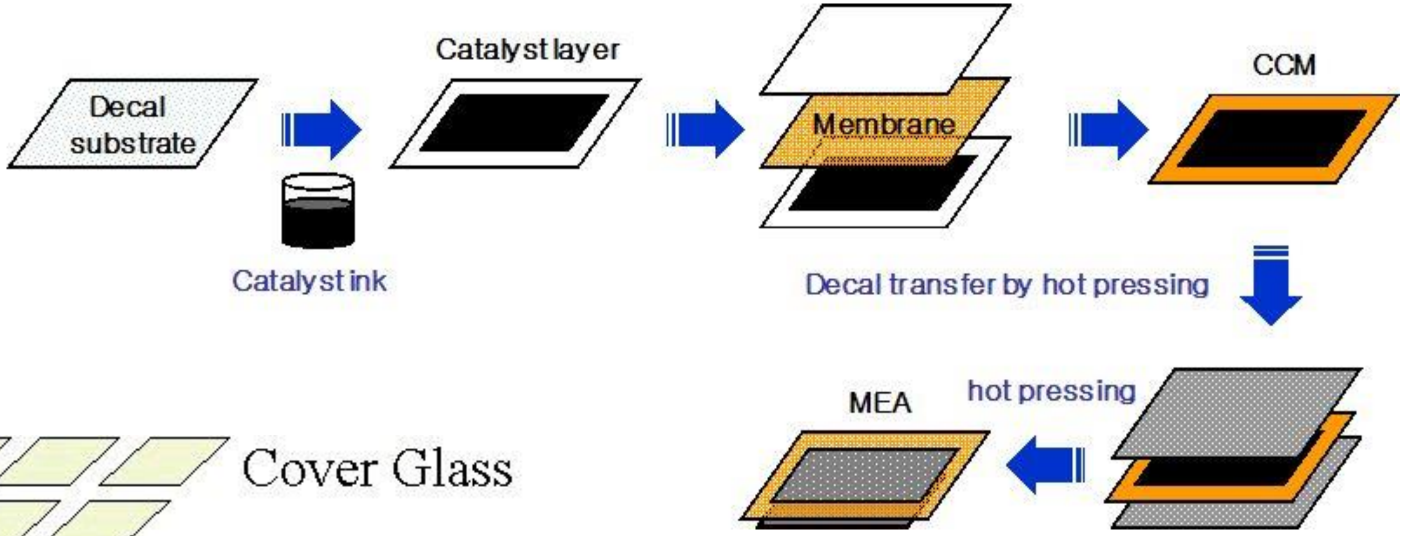


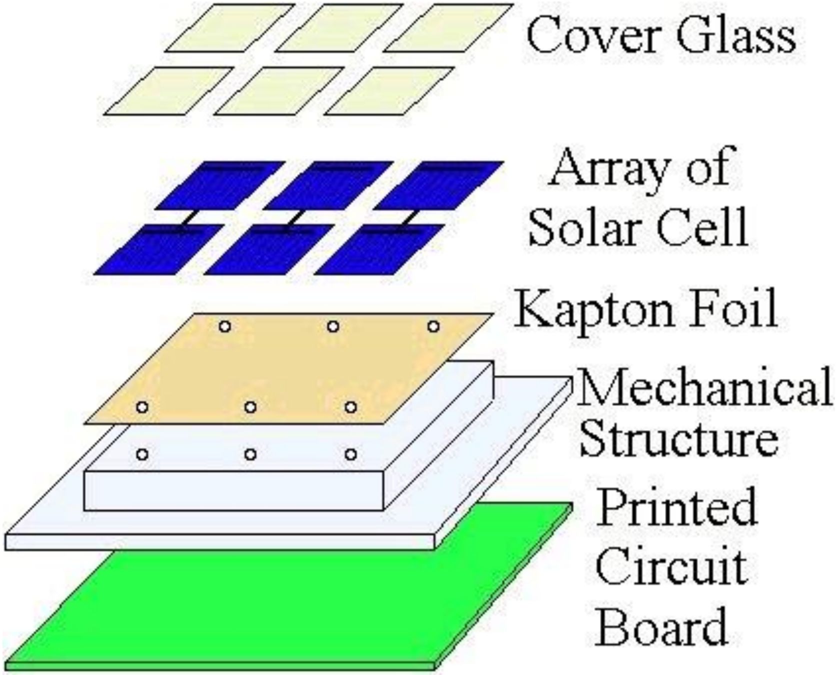
- Less structural support required, due to 1/3 g
  - **What does that look like?**



- Vapor vs. Liquid (Water) Feed?
  - **Liquid:** Failures due to gravity
  - **Vapor:** Failures due to pressure, but aspect ratio can alleviate this
- Compressor is "free" mass (scroll pump from MOXIE)
  - **Reactants:** CO_2, water (vapor)
  - **Products:** O_2, CO (or other)
- **Can the device handle temperature cycles/swings (esp. Nafion)?**

ULW PEC Device/System





Cell/Module Bill of Materials

Nearly everything "cost" ~1 g/m^2 per μm thick = 1 g/mL

- Containment
  - Gorilla Glass (25 μm) 60 g/m^2
  - <u>or</u> HDPE (75 μm) 75 g/m^2

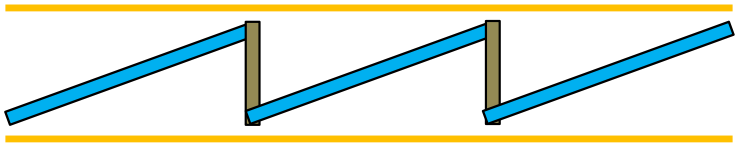
  %T = 95, leak rate = 45 g H_2/m^2/year (3.5% of H_2 produced)[i]

- PV *(assume η_{STH} = 10% at 1 Sun on Earth)*
  - PV Materials and Contacts 20 g/m^2
  - Kapton Support (15 μm) 15 g/m^2

- MEA
  - Catalysts (2 mg/cm^2) 20 g/m^2
  - C Fiber (25 μm) 25 g/m^2
  - Nafion (50 μm) 50 g/m^2
  - C Fiber (25 μm) 25 g/m^2
  - Catalysts (2 mg/cm^2) 20 g/m^2

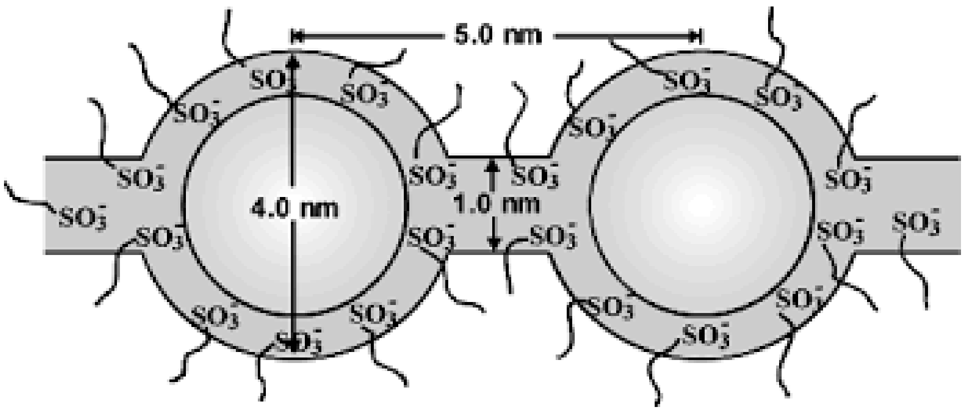
+ 20% for structural support
+ *x*% for pipes, control system, etc.

One person's propellant requires ~1000 m^2, which here equates to a (370 + *y*) kg payload (<u>< 0.5 mt</u>)!



[i] Directed Technologies, Inc., DOE Report, **2009** & Pinaud, …, Ardo, …, Jaramillo, *Energy Environ. Sci.*, **2013**, *6*, 1983

Teflon (PTFE) / Gore-Tex / Nafion



Mauritz & Moore, *Chemical Reviews*, **2004**, *104*, 4535

http://www.nafion.mysite.com/

$$(m+n)CF_2{=}CF_2 + n\ CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F \xrightarrow{\text{initiator}}$$

TFE FC-141

$$\longrightarrow [-(CF_2CF_2-)m-CFCF_2-]n$$

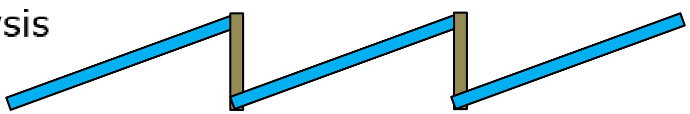
O (side chain attached to CF)

$CF_2CF(CF_3)OCF_2CF_2SO_2F$

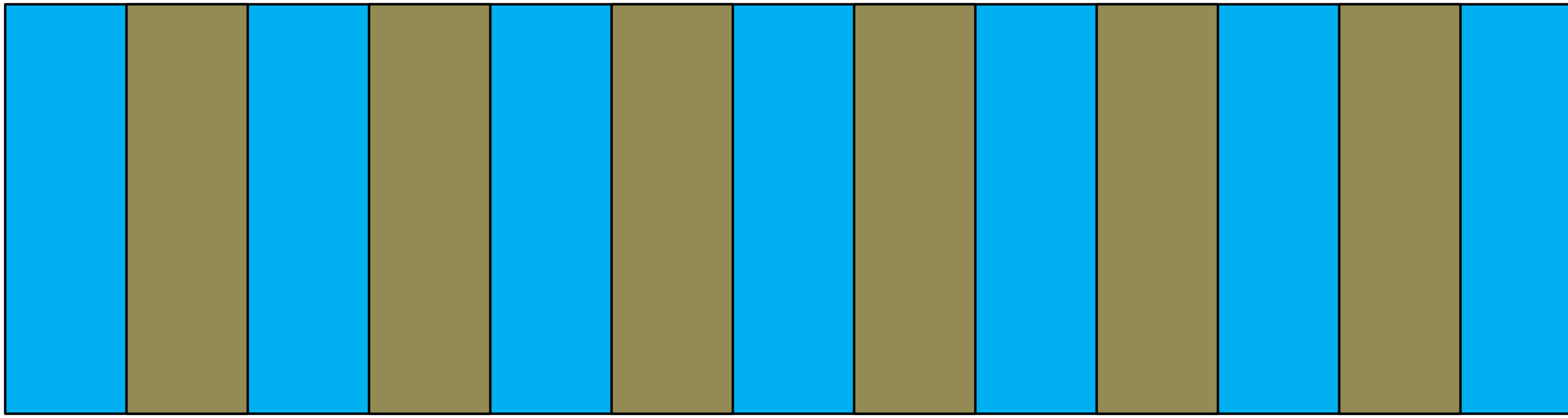
Nafion–SO_2N-CH_2CH_3 *(hydrophobic)*

-hydrolysis

$\sim OCF_2CF_2SO_3H$



Teflon (PTFE) / Gore-Tex / Nafion



initiator

$(m+n)CF_2{=}CF_2 + n\ CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F \longrightarrow$

TFE FC-141

$\longrightarrow [-(CF_2CF_2-)m-CFCF_2-]n$

| (side chain) O | (side chain)

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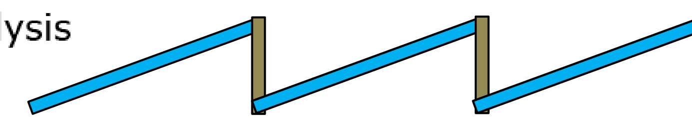
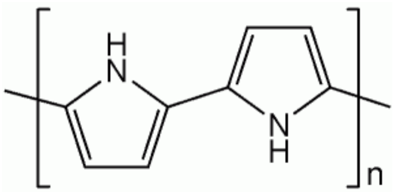


Teflon (PTFE) / Gore-Tex / Nafion

Accession Number : ADA159708

Title : Electronically Conductive Composite Polymer Membranes.

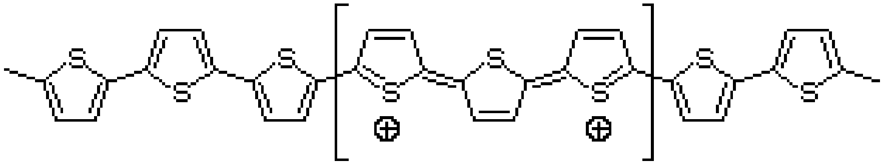


Descriptive Note : Technical rept.,

Corporate Author : TEXAS A AND M UNIV COLLEGE STATION DEPT OF CHEMISTRY

Personal Author(s) : Penner,R M ; Martin,C R

PDF Url : ADA159708



Report Date : 20 Sep 1985

Pagination or Media Count : 31

Abstract : We have recently described the preparation and properties of ionically conductive Nafion-impregnated Gore-tex (NIGT) composite membranes. In this paper we describe electronically conductive composite membranes prepared by electropolymerizing either pyrrole or thiophene within the ionically conductive NIGT membrane. These composites have the mechanical properties of the host membrane yet the electronic conductivity of the NIGT/polypyrrole composite membrane is essentially identical to that of polypyrrole. For comparison, we have also attempted to electropolymerize pyrrole in nafion membranes and films and in bare Gore-tex and poly(vinyl chloride)-impregnated Gore-tex. We have found that the rate of polymerization of pyrrole at a NIGT-coated Pt electrode is higher than the rate at bare Pt. The origins of this rate enhancement are probed.

Descriptors : *POLYMERS, *ELECTRICAL CONDUCTIVITY, *MEMBRANES, MECHANICAL PROPERTIES, OPTIMIZATION, COMPOSITE MATERIALS, POLYMERIZATION, RATES, ELECTRONS, PYRROLES, ION EXCHANGE RESINS, IONIC CURRENT, POLYVINYL CHLORIDE, THIOPHENES

Subject Categories : Physical Chemistry
Plastics

Distribution Statement : APPROVED FOR PUBLIC RELEASE

Summary

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- Metrics (W/kg, kg/m^2)
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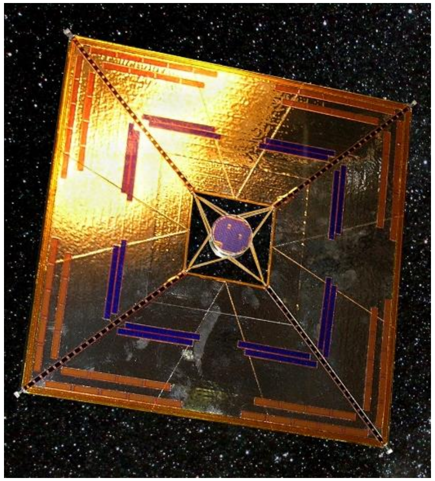

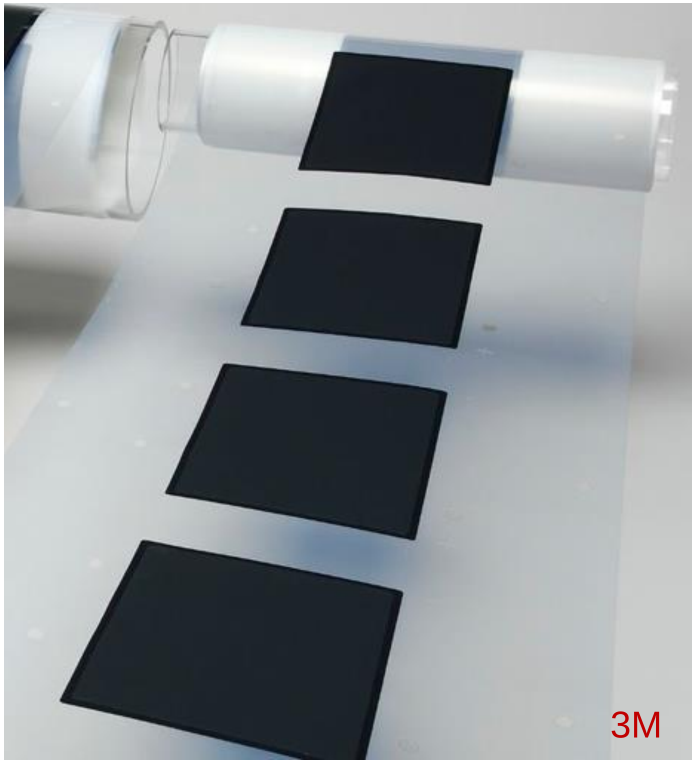

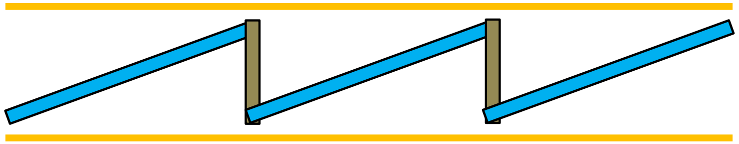

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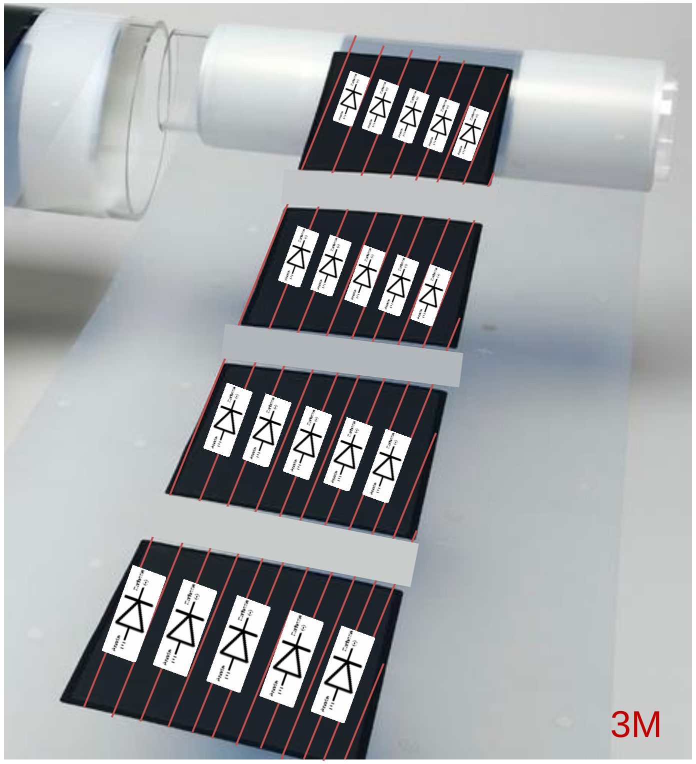
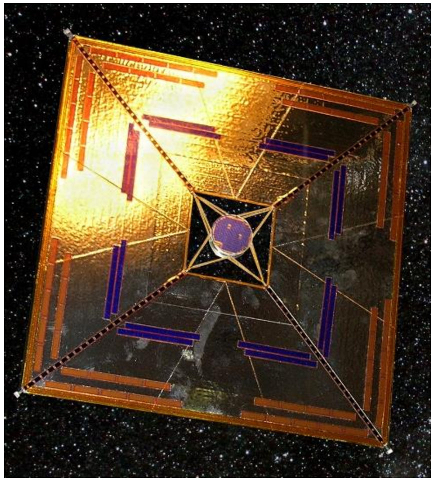
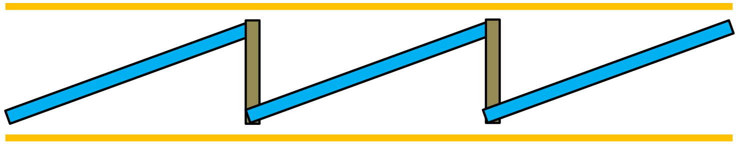




5-6x photocurrent increase
AM0, no dust, capacity factor
small transmission loss
Heat ice

(need AC–DC conversion)



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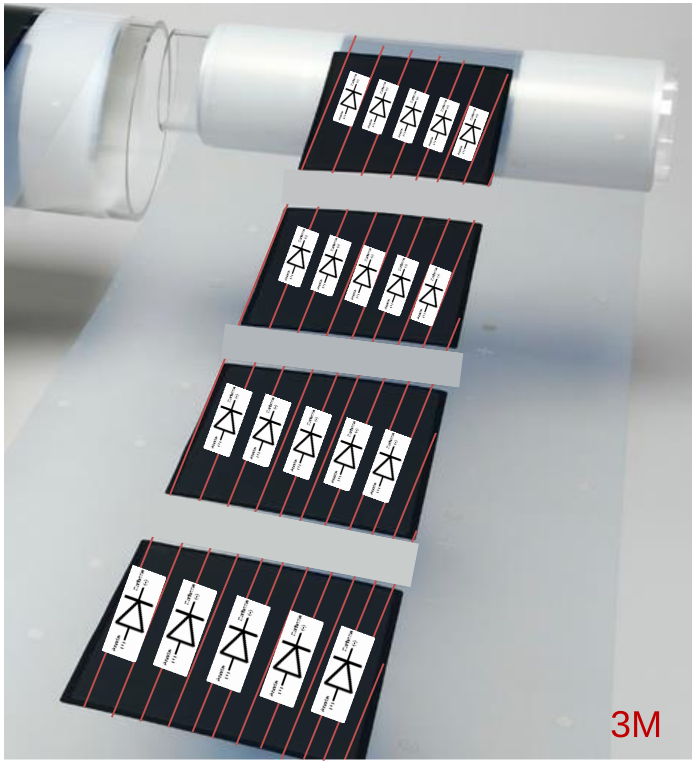

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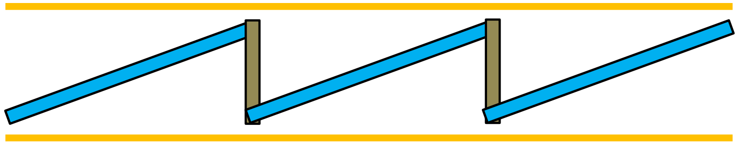
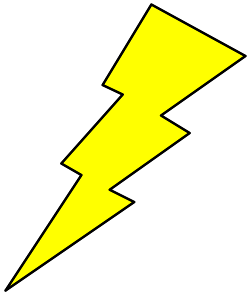


<u>Waterless resources</u>
- Nafion + catalytic water
- Ionic liquid gel at cathode
- Carbonate cycle

PS 2: Motivation for other feedstocks



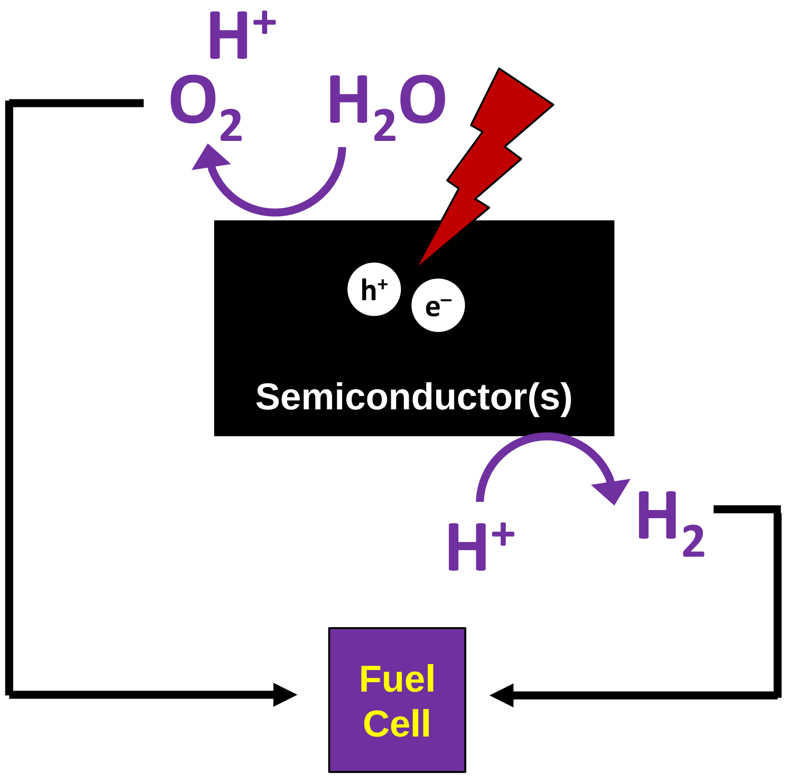
Coral 2, Mid-Pacific Conference Center, Hilton Hawaiian Village

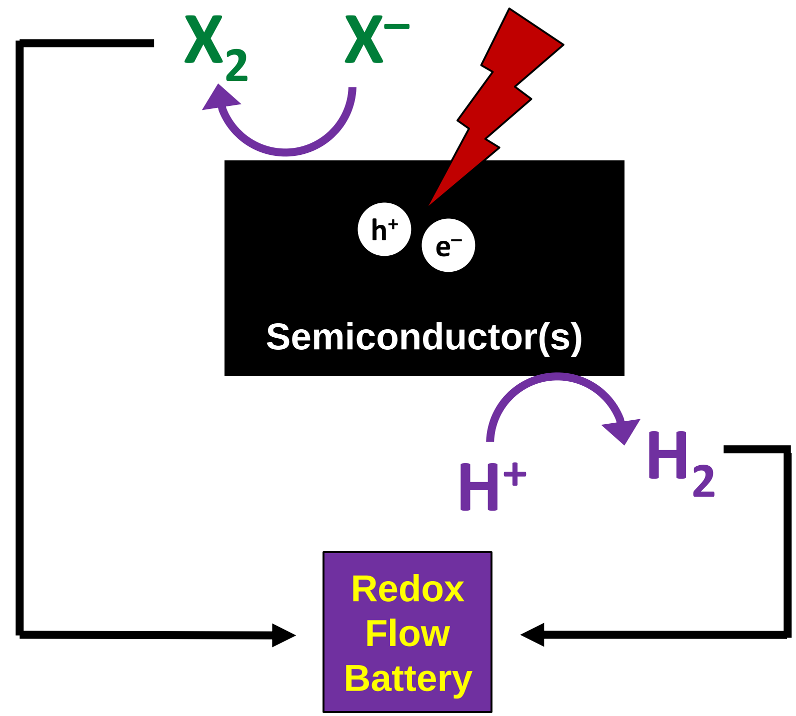
Flow Battery Cell

Co-Chairs: Adam Weber and Trung Nyugen

Time	Progr#	Title and Authors
14:00	392	Performance Improvement of a Hydrogen-Bromine Flow Battery K. Cho, A. Weber, Q. He, P. Ridgway, V. Battaglia, and V. Srinivasan (Lawrence Berkeley National Laboratory)
14:20	393	Recent Progress in Redox Flow Battery Research and Development at Pacific Northwest National Lab W. Wang, Q. Luo, Z. Nie, M. Vijayakumar, X. Wei, B. Li, F. Chen, B. Chen, Y. Shao, G. Xia, L. Li, and Z. Yang (Pacific Northwest National Laboratory)
14:40	394	New Discharge/Charge Performance Data for a H_2-Br_2 Flow Battery V. Yarlagadda and T. V. Nguyen (The University of Kansas)
15:00	395	Halogen Flow Batteries for Grid-Scale Electricity Storage B. Huskinson, S. Mondal, J. Rugolo, and M. J. Aziz (Harvard School of Engineering and Applied Sciences)
15:20	396	Grid-Scale Energy Storage Requirements and the Potential for Halogen-Based Flow Batteries J. Rugolo, B. Huskinson, and M. J. Aziz (Harvard School of Engineering and Applied Sciences)
15:40		Intermission (20 Minutes)
16:00	397	Aqueous Semi-Solid Flow Cell Z. Li, P. Limthongkul, W. Carter, and Y. Chiang (Massachusetts Institute of Technology)
16:20	398	Hydrogen Bromine Redox Flow Battery Cell Performance Study Y. Bai (The University of Tennessee Knoxville), A. B. Papandrew, and T. A. Zawodzinski Jr. (The University of Tennessee)
16:40	399	Characterization of Vanadium Redox Flow Batteries: An AC Impedance Spectroscopy Study C. Sun (Oak Ridge National Laboratory), D. S. Aaron (The University of Tennessee Knoxville), A. Papandrew, and T. A. Zawodzinski Jr. (The University of Tennessee)
17:00	400	Performance Enhancement, Limitations, and Diagnostics of Vanadium Redox Flow Batteries J. T. Clement, A. M. Pezeshki, Q. Liu, A. B. Papandrew, A. Turhan, T. A. Zawodzinski Jr., and M. M. Mench (The University of Tennessee)
17:20	401	Coulombic Efficiency of a Vanadium Redox Flow Cell X. Gao, R. Lynch, M. Leahy, and D. Buckley (University of Limerick)

Maximizing round-trip efficiency





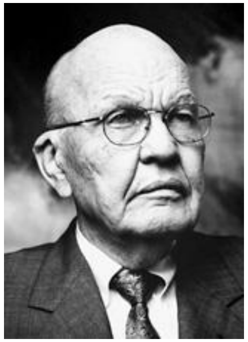
Difficult 4-e⁻ PCET reaction, *that nature figured out*

Facile 2-e⁻ ET reaction, *that we can do today*

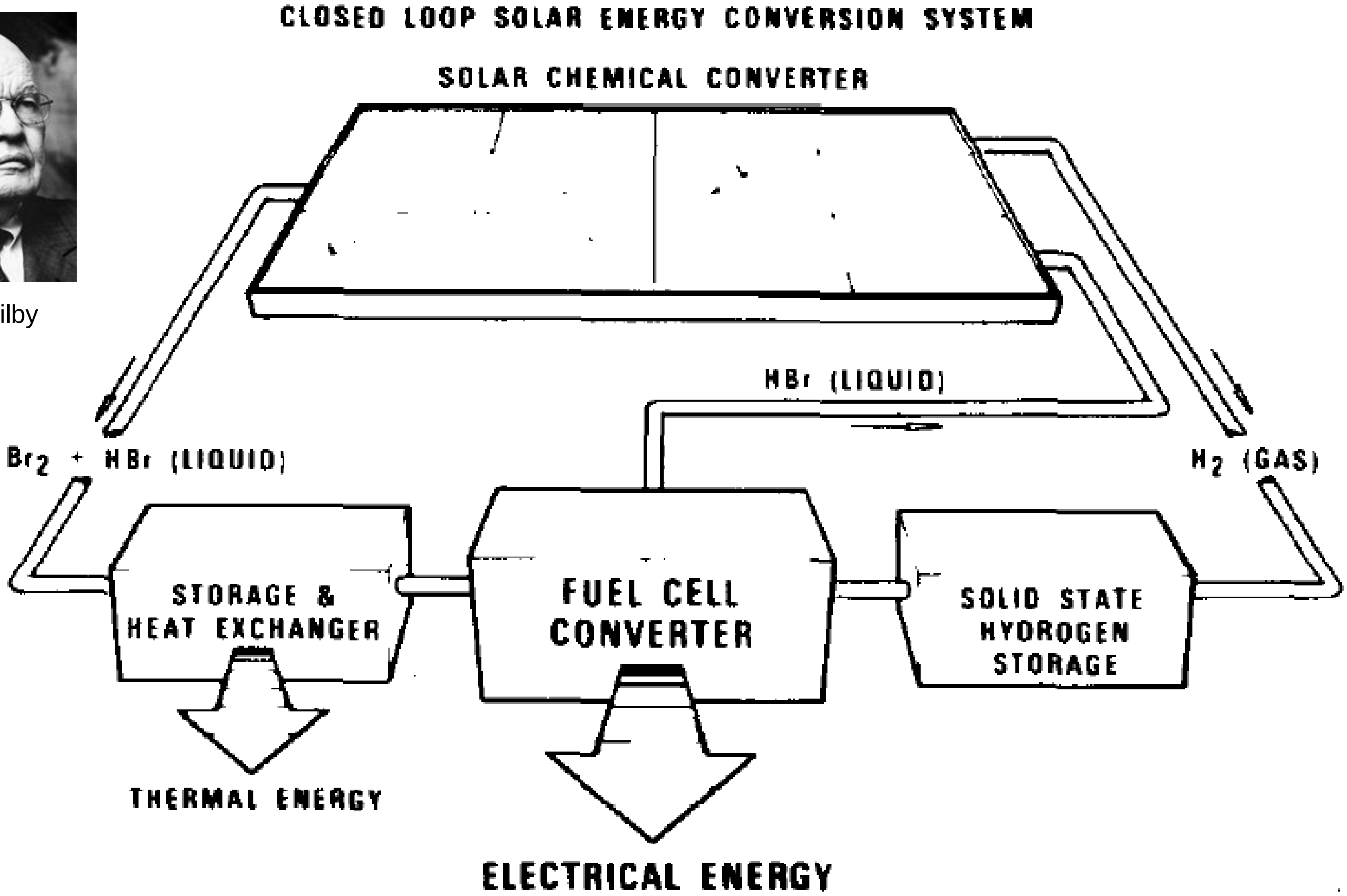
GOAL: Efficiently, inexpensively, and robustly store photon energy for use when dark

Johnson, *IEEE IEDM* (**1981**) 81-2–6; McKee, *IEEE Trans.* (**1982**) *CHMT-5*, 336–341; Luttmer & Trachtenberg, *J. Electrochem. Soc.* (**1985**) *132*, 1312–1315

Before the TI82 calculator there was ...



Jack Kilby



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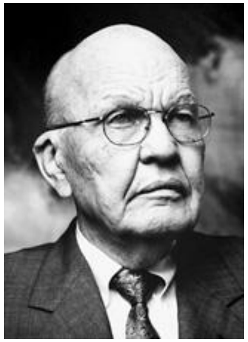

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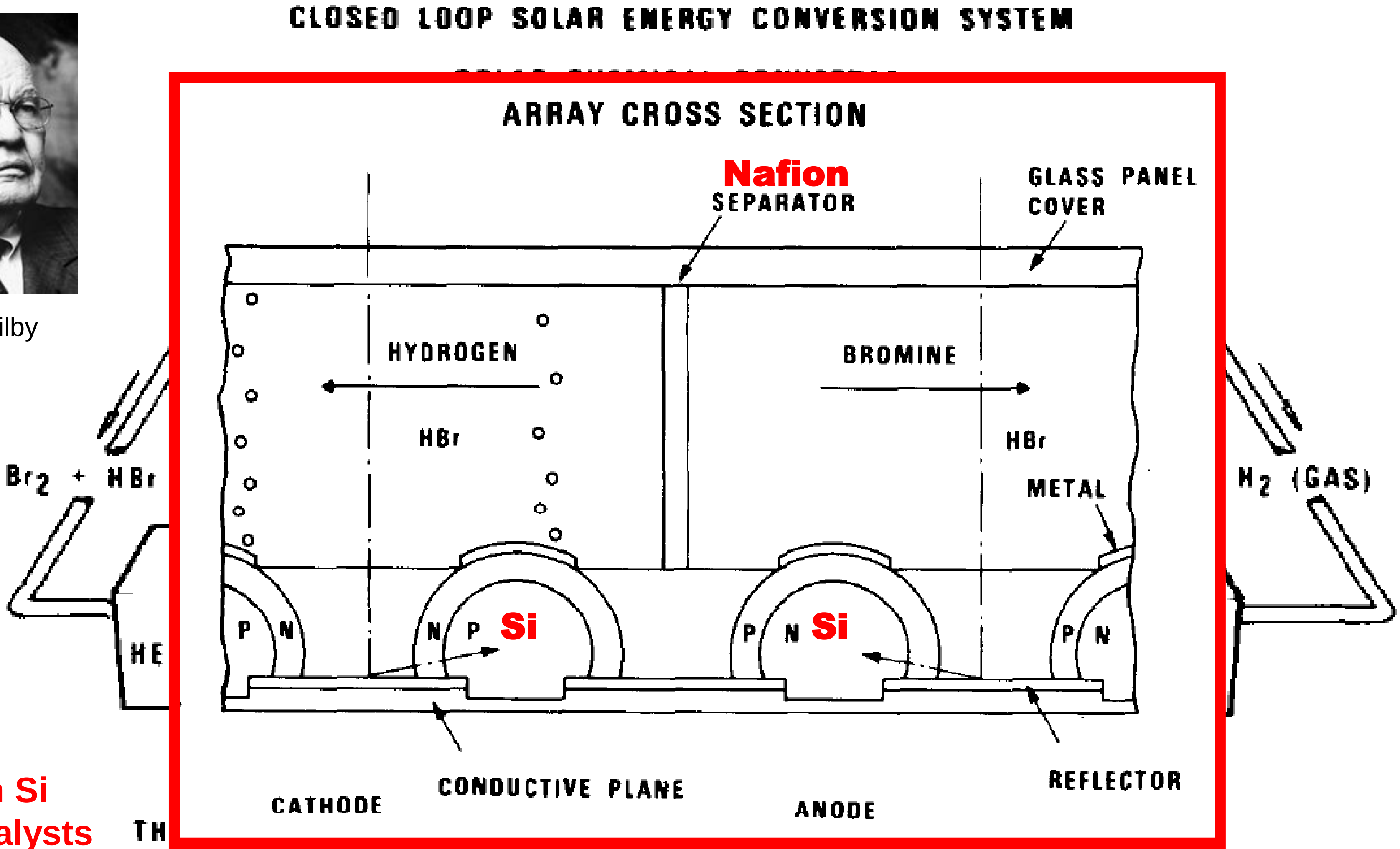
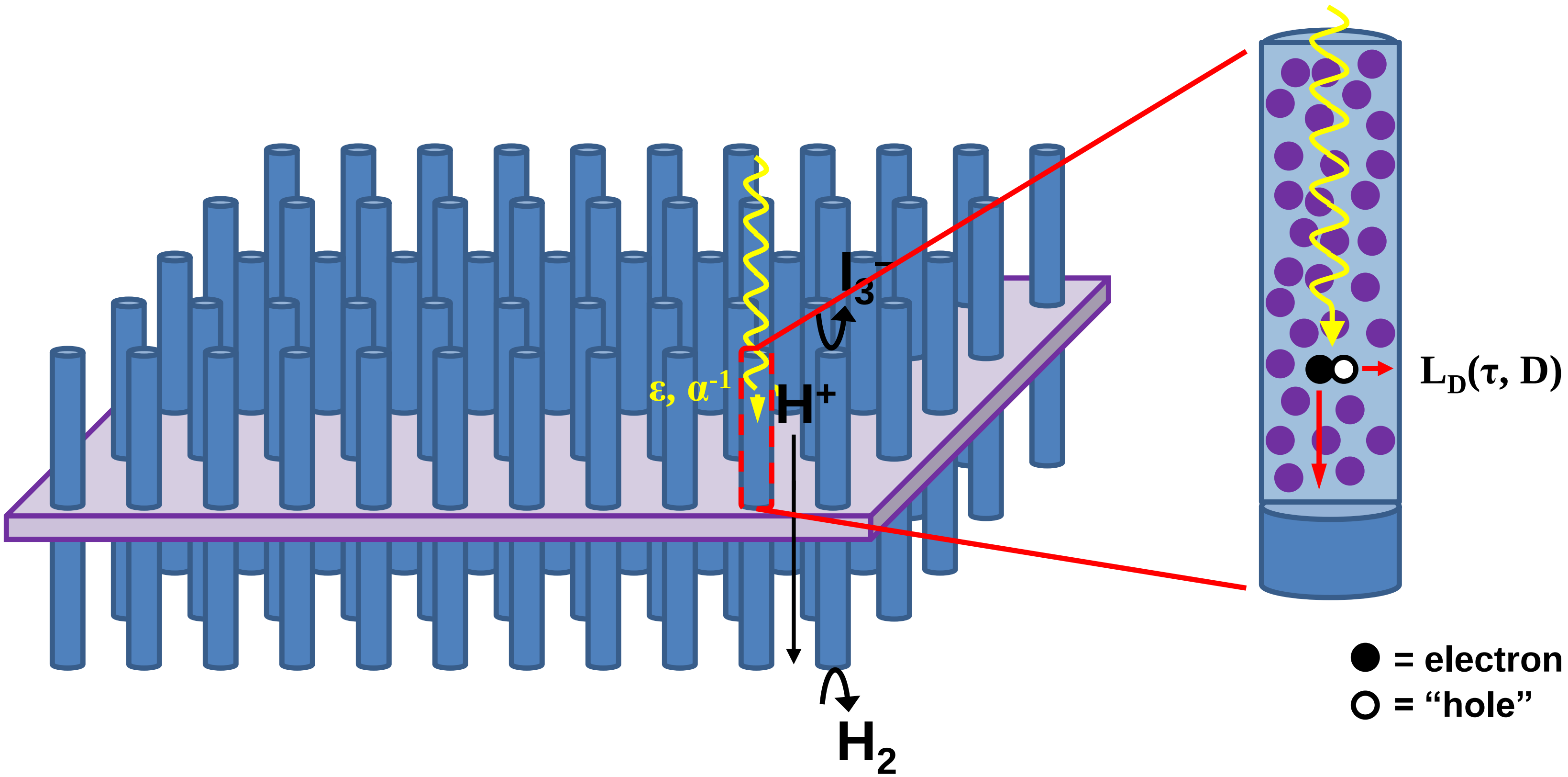


~100 μm Si
Pt/Ir catalysts
$\eta_{STF} \approx 8\%$
$\eta_{full} \approx 5\%$

$2\ H–Br \rightarrow H_2 + Br_2/Br_3^-$ $\Delta E^o = -1.05\ V$

Johnson, *IEEE IEDM* (**1981**) 81-2–6; McKee, *IEEE Trans.* (**1982**) *CHMT-5*, 336–341; Luttmer & Trachtenberg, *J. Electrochem. Soc.* (**1985**) *132*, 1312–1315

The Lewis Group approach



- **Charge carrier collection**
- Voltage drop/loss in electrolyte (= iR)
- Crossover of H_2/O_2
- Flexibility

Microwire arrays

<u>Chemical Vapor Deposition Protocol</u>

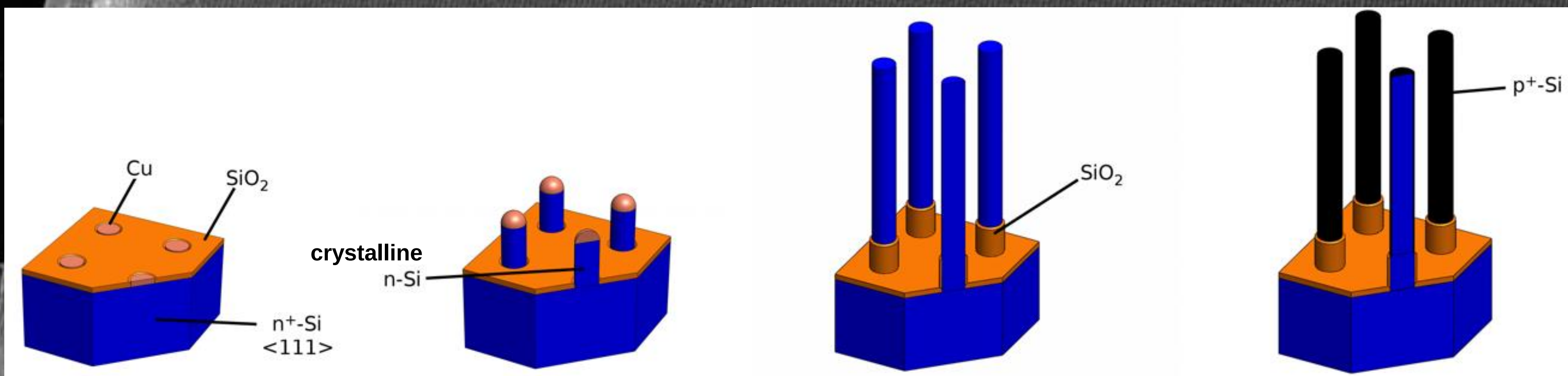
Cu VLS growth catalyst, square 3 x 7 µm pattern

1000 ° C H_2, $SiCl_4$, PH_3, and/or BCl_3

Post processing to remove Cu and mask base

Radial pn junctions via diffusion doping

Doped 1E17 cm^{-3} with > 5E19 cm^{-3} emitters

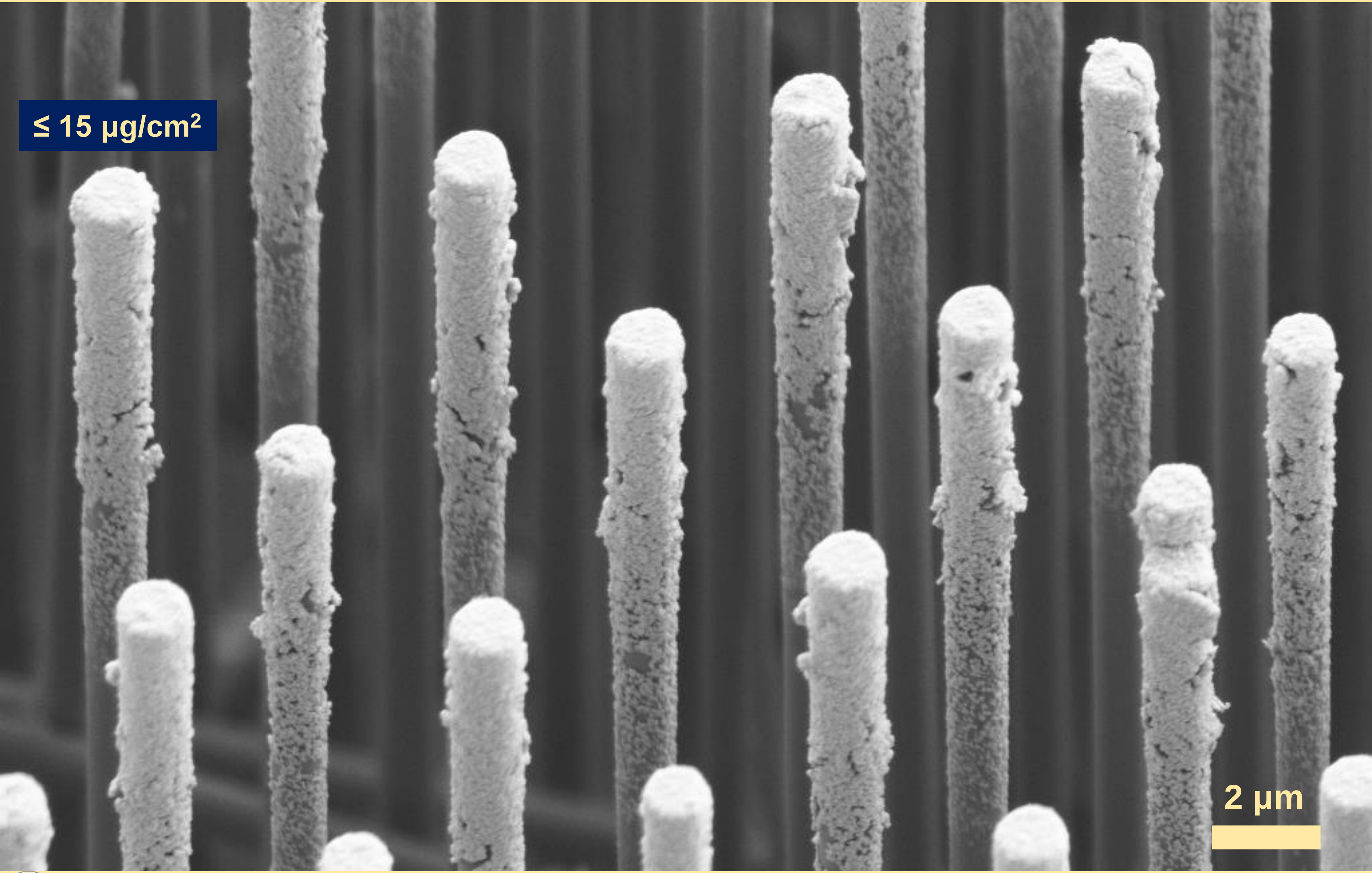


Boettcher, …, Atwater & Lewis, *Science* (**2010**) *327*, 185–187

sample region shown here is $^1/_{10}{}^{th}$ of an inch wide

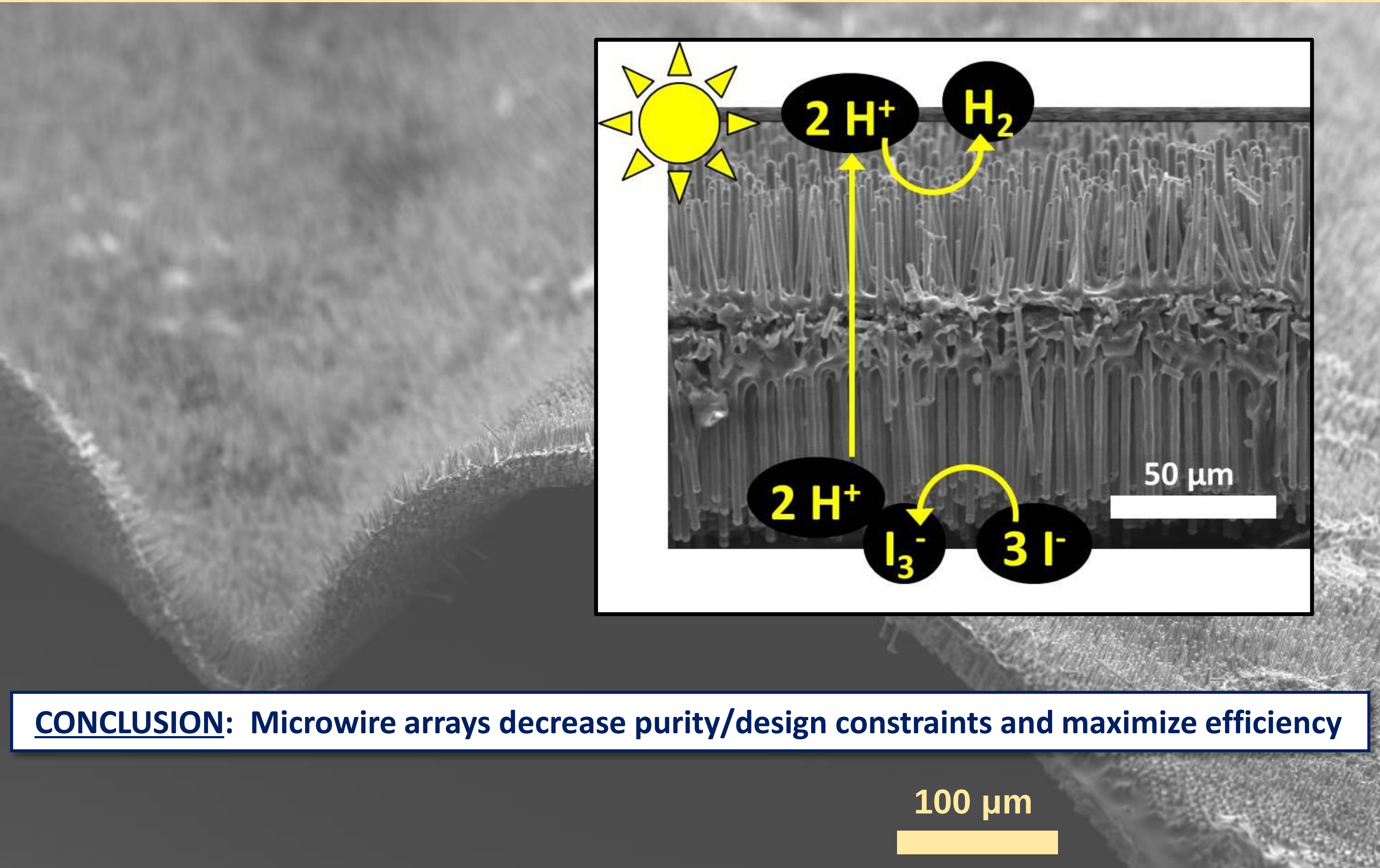
Kayes, Atwater & Lewis, *J. Appl. Phys.* (**2005**) *97*, 114302-11

Interfaced catalysts



Boettcher, Warren, …, Atwater & Lewis, *J. Am. Chem. Soc.* (**2011**) *133*, 1216–1219
McKone, Warren, …, Lewis & Gray, *Energy Environ. Sci.* (**2011**) *4*, 3573–3583

Semiconductor–Separator composite



<u>CONCLUSION</u>: Microwire arrays decrease purity/design constraints and maximize efficiency

Ardo, Park, Warren & Lewis, , *Energy Environ. Sci.* (**2015**) *8*, 1484–1492
Spurgeon, …, Kohl & Lewis, *Energy Environ. Sci.* (**2011**) *4*, 1772–1780

The Tandem

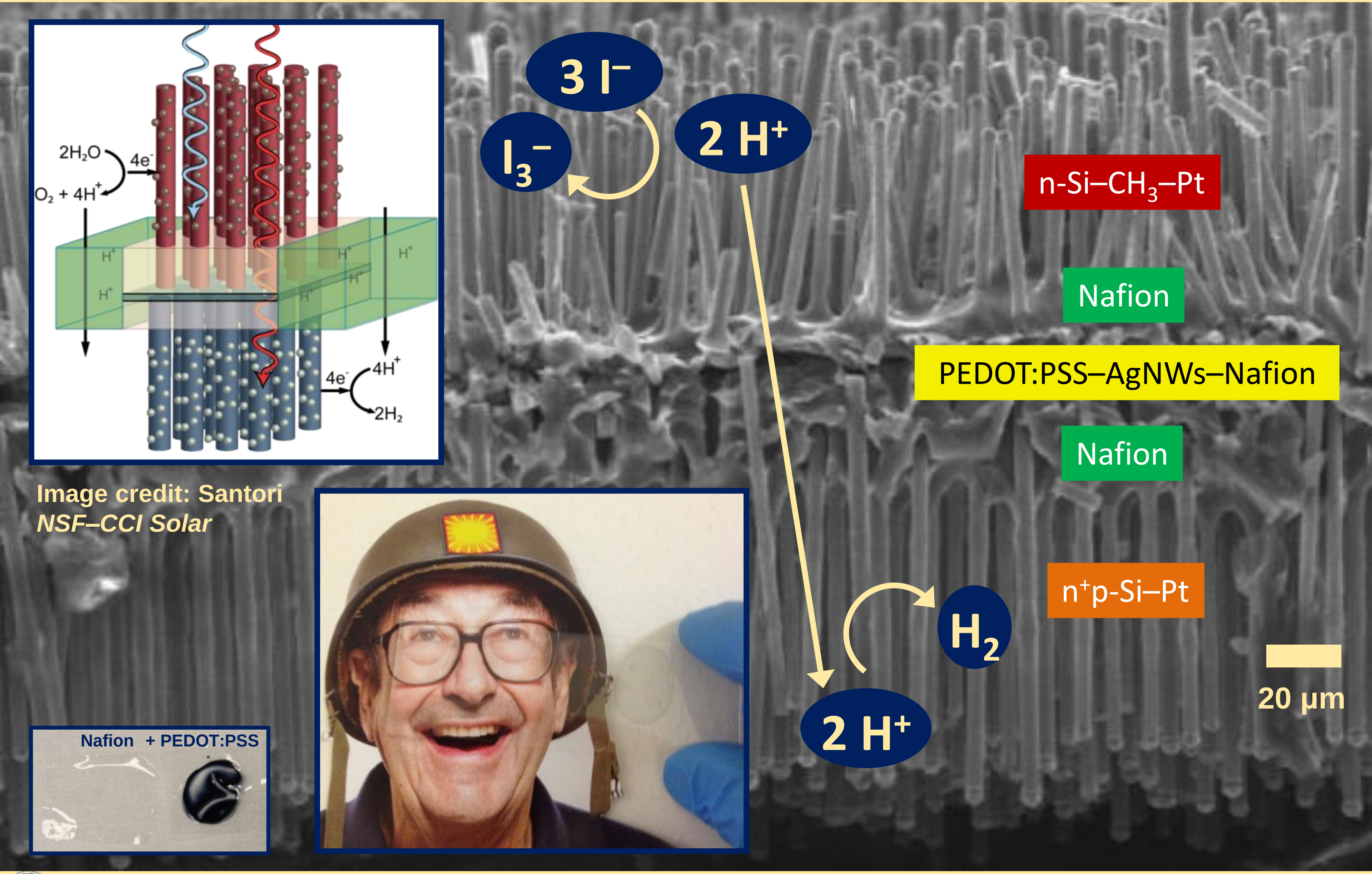
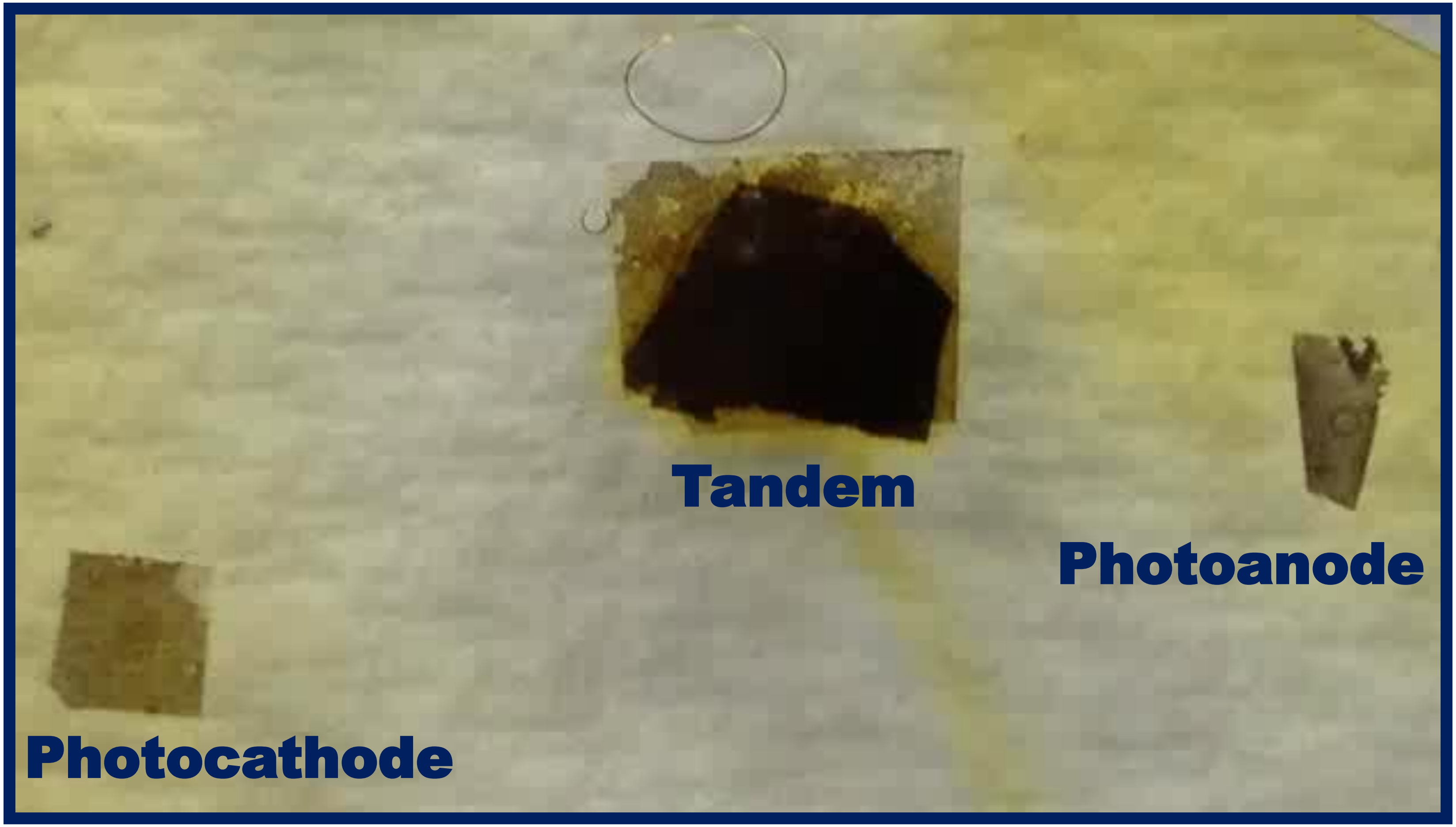


Image credit: Santori
NSF–CCI Solar

Functioning peeled devices



Ardo & Lewis, *Full Patent (submitted), California Institute of Technology* (**2013**)

PS 3: Electrolyzer (Fuel cell) requirements

Can I spell "fveI ce11"?

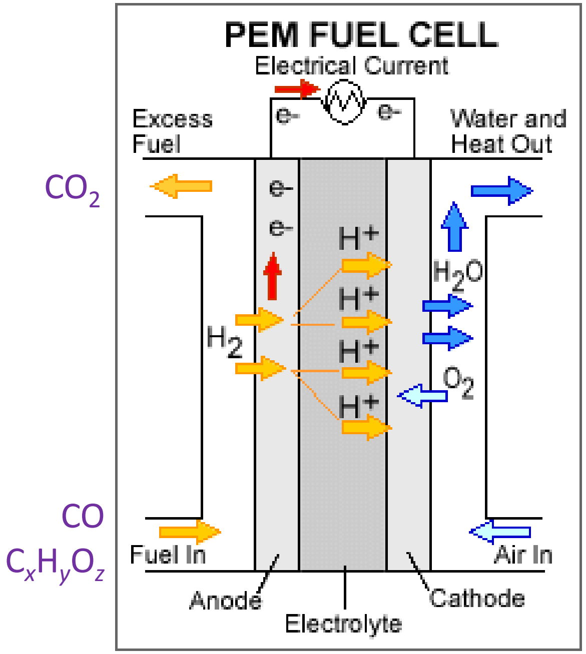
ANSWER: **I'm not certain.**

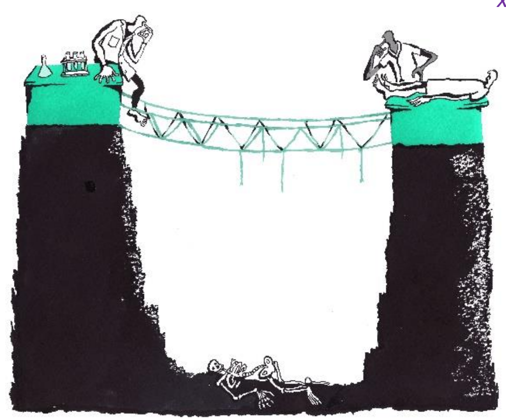
What chemical phase (G/L/S) is required?

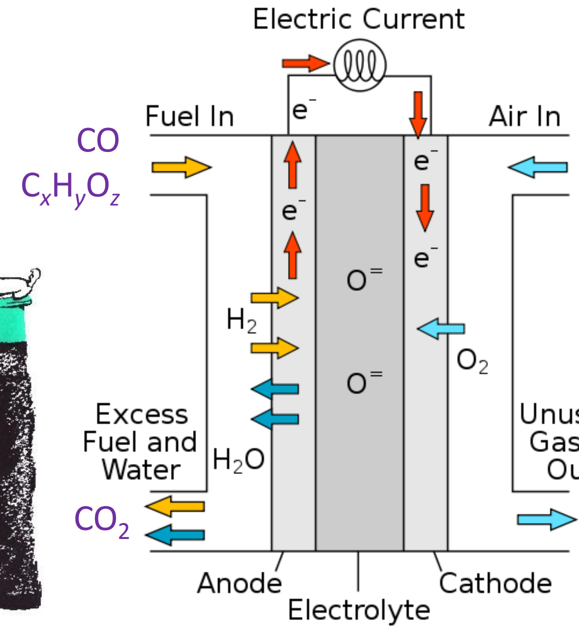
What chemical purity is required?

Can it handle variable power input?

Phase requirements







"MOXIE," backward

< 100 °C

> 700 °C

- Electrocatalysis/membrane dominates V_{loss}
- Need pure H_2 feed stream (see next slide)
- CO poisons H_2 catalyst (see next slide)
- Nafion transports CO slower than O_2
- Need an H^+ source like H_2O (or AEM)

- Ohmic drop dominates V_{loss}
- Easy to make reversible
- Dirty feeds permissible
- In situ reforming to H_2 / $C_xH_yO_z$

  (possibly some coking)

Purity requirements

Ayers, Kathy <kayers@protononsite.com> Today at 6:52 AM

To Shane Ardo

I don't know that much about SOFC/SOEC purity requirements specifically but would guess they are considerably relaxed due to the high temp. SOFCs are fuel flexible and certainly more tolerant to CO, I'm not sure about things like sulfur or certain hydrocarbons, there could be problems with coking. SOECs are based on steam so I would imagine water quality wouldn't be that much of an issue other than fouling whatever vessel was being used to heat the water. Not sure about typical feed pressures either although I don't think solid oxide does very well at differential pressure.

PEM is very sensitive to sulfur and CO, at ppm levels (platinum poisoning). To my knowledge, typically fuel cells take 25-50 psi hydrogen and oxygen (or clean air) input. Our water spec for electrolysis is Type II ASTM, which is 1 megaohm or higher resistivity and also includes specs on silicate and TOCs.

That's my off the top of my head answer but feel free to ask for more since I'm not sure how much detail Wiki will have on actual operational characteristics.

H_2 purity standard (ISO 14687-2:2012): > 99.97 % H_2; < 0.2 ppm CO; < 4 ppb H_2S

See NREL's database on PEM fuel cell contaminants: http://www.nrel.gov/hydrogen/system_contaminants_data/

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I don't know that much about SOFC/SOEC purity requirements specifically but would guess they are considerably relaxed due to the high temp. SOFCs are fuel flexible and certainly more tolerant to CO, I'm not sure about things like sulfur or certain hydrocarbons, there could be problems with coking. SOECs are based on steam so I would imagine water quality wouldn't be that much of an issue other than fouling whatever vessel was being used to heat the water. Not sure about typical feed pressures either although I don't think solid oxide does very well at differential pressure.

PEM is very sensitive to sulfur and CO, at ppm levels (platinum poisoning). To my knowledge, typically fuel cells take 25-50 psi hydrogen and oxygen (or clean air) input. Our water spec for electrolysis is Type II ASTM, which is 1 megaohm or higher resistivity and also includes specs on silicate and TOCs.

That's my off the top of my head answer but feel free to ask for more since I'm not sure how much detail Wiki will have on actual operational characteristics.

DOE: electrolyzed to ~20 bar and ~700 bar in cars

	Type I	Type II	Type III	Type IV
Electrical conductivity, max, µS/cm at 298 K (25°C)	0.056	1.0	0.25	5.0
Electrical resistivity, min, Mcm at 298 K (25°C)	18	1.0	4.0	0.2
pH at 298 K (25°C)	*A*	*A*	*A*	5.0 to 8.0
Total organic carbon (TOC), max, µg/L	50	50	200	no limit
Sodium, max, µg/L	1	5	10	50
Chlorides, max, µg/L	1	5	10	50
Total silica, max, µg/L	3	3	500	no limit

http://www.astm.org/DATABASE.CART/HISTORICAL/D1193-99E1.htm

CO interactions with Nafion

ELSEVIER

Sensors and Actuators B: Chemical

Volume 35, Issues 1–3, September 1996, Pages 119-123

Proceedings of the Sixth International Meeting on Chemical Sensors

Extremely stable Nafion based carbon monoxide sensor

P.D van der Wal, N.F de Rooij, M Koudelka-Hep

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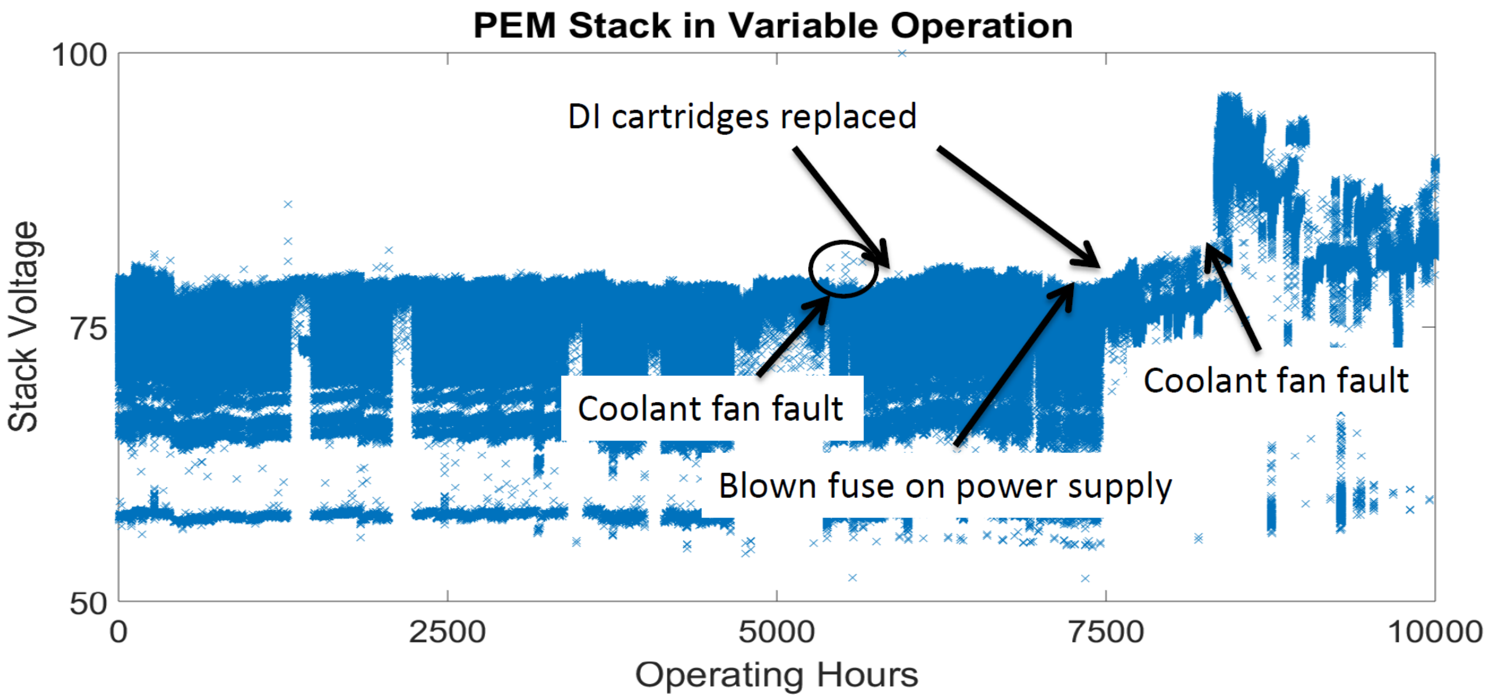
Abstract

Carbon monoxide sensors using Nafion solid polymer electrolyte are described. Dry Nafion sensors showed stability problems; on the other hand sensors equipped with a water reservoir (wet Nafion sensors) were extremely stable. The proposed manufacturing technology, compatible with hybrid technology is suitable for cheap mass fabrication.

http://www.sciencedirect.com/science/article/pii/S0925400597800408

Variability performance of electrolyzer

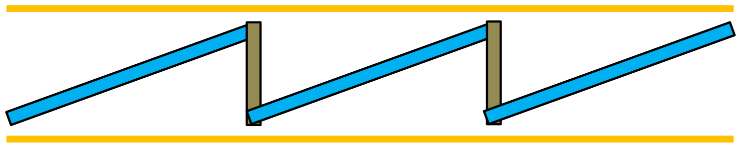


Peters (NREL)

See NREL document from DOE-EERE-FCTO-AMR's website

https://www.hydrogen.energy.gov/annual_review16_fuelcells.html#performance

Summary



- **~0.5 mt "today"... that payload seems reasonable!**
- **When do we start testing prototypes on Earth?**
- Transmit power to Mars using microwaves and cell-phone-sized receivers in catalyst layers (with rectifiers)
- Alternative electrolytes could be useful
- Alternative redox couples could be useful
- Pure chemical feeds could be useful