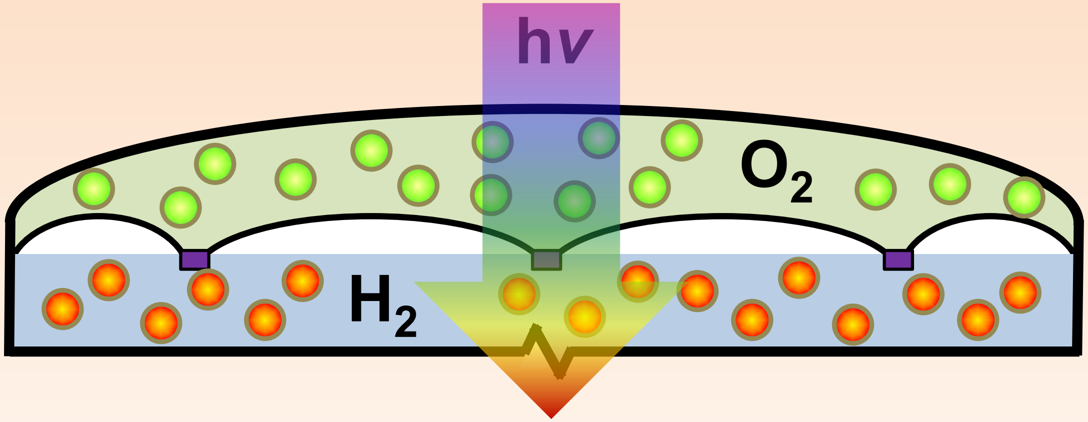
PD125

Tandem particle-slurry batch reactors for solar water splitting

Shane Ardo

University of California, Irvine



Thursday, June 14, 2018

US DOE, EERE, FCTO, Annual Merit Review

Overview

Project Timeline

- Start date: August 1, 2015
- New end date: June 30, 2018

  (35-month period of performance)

Project Budget

Total budget:	$1,248,063
– Federal funds:	$ 993,759
– UCI cost share:	$ 254,304

- Funding by year (UCI only)

– Years 1 – 2 spent:	$ 571,658
– Years 1 – 2 budget:	$ 726,324
– Year 3 spent*:	$ 109,595
– Year 3 budget:	$ 0

* as of 3/31/2018

Barriers Addressed

- (AG) Integrated Device Configurations
- (AH) Reactor Designs
- (AI) Auxiliary Materials
- (AJ) Synthesis and Manufacturing

Partners / Collaborators

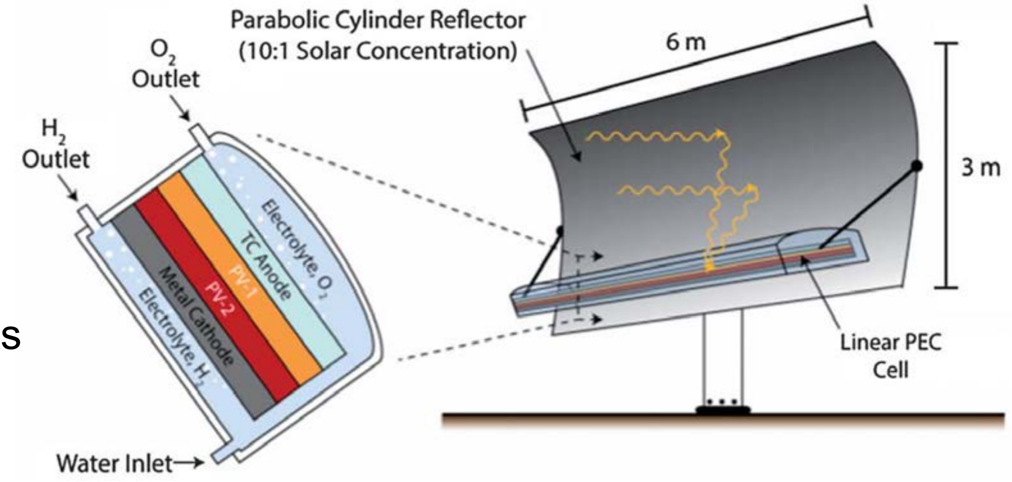
- Device-physics modeling and simulation contributors
  - **Lawrence Berkeley National Laboratory & JCAP** (Adam Weber, *sub-recipient*)
  - **California Institute of Technology & JCAP** (Chengxiang Xiang, *sub-contracted advisor*)
- Materials contributors
  - **Tokyo University of Science** (Akihiko Kudo, *unfunded*)

Relevance: Motivation

Wafers (Type 4) and Particles (Type 2)

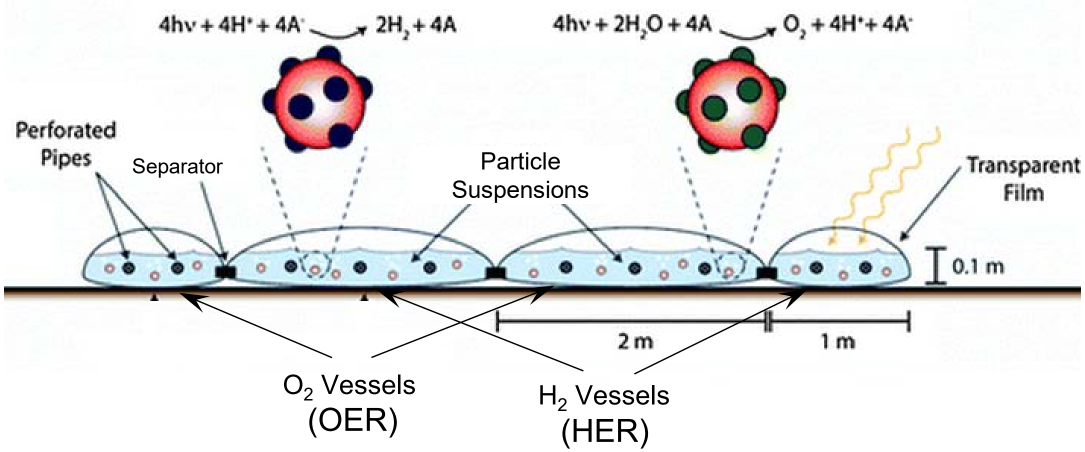
Fixed-electrode Design

- Wafers immersed in electrolyte
- Optical concentration of ≥ 10x
- Could meet MYRD&D targets
  - High-efficiency materials
  - Large reductions in materials costs



Particle-slurry Design *(this work)*

- Two particle suspensions
- Side-by-side plastic "baggies“
- Porous via allows mixing of the molecular redox shuttle (A/A⁻)
- Requires many pumps & pipes
- Could meet MYRD&D targets
  - Less stringent requirements
  - TRL is very low



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

Relevance: Concept

Project Objective: **Experimentally validate** a *new design* for scalable solar-H_2 technologies using laboratory-scale prototype particle suspension reactors

August 2016 Objective: **Numerically demonstrate** that the *new reactor design* can sustain a ≥ 1% solar-to-hydrogen (STH) conversion efficiency

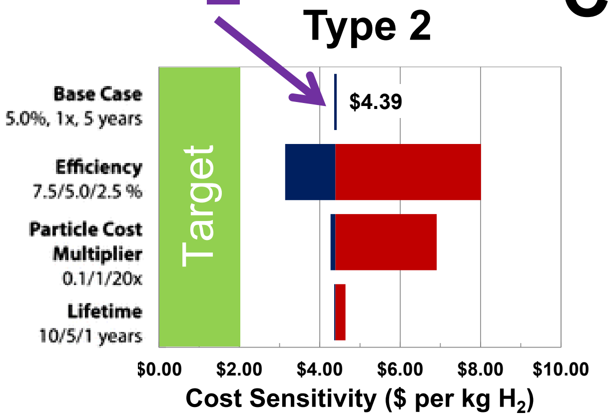
	MYRD&D Targets for a Type 2 Reactor				
Characteristics	**2011**	**2015**	**Proposed**	**2020**	**Ultimate**
H_2 Cost (\$/kg)	N/A	28.60	20.00	4.60	2.10
η_{STH} (%)	N/A	1.0	1.0	5.0	10

DOE Barriers	**Project Goal**
(AJ) Synthesis and Manufacturing **(AG) Integrated Device Configurations**	• Synthesize state-of-the-art light-absorber nanoparticle photocatalysts as powders, inks, and thin films • Electrodeposit electrocatalysts on light-absorber nanoparticle photocatalysts using solid-state chemistry, photo(electro)deposition, and bipolar electrochemistry
(AH) Reactor Designs	• Model and simulate device physics, techno-economics, and efficiency limits for new tandem two-compartment particle suspension reactors • Fabricate model reactors with *in situ* monitoring capabilities, and assess redox shuttle transport rates
(AI) Auxiliary Materials	• Identify optimal redox shuttles based on optical transparency, rates of mass transport, and efficiency for selective electrocatalysis

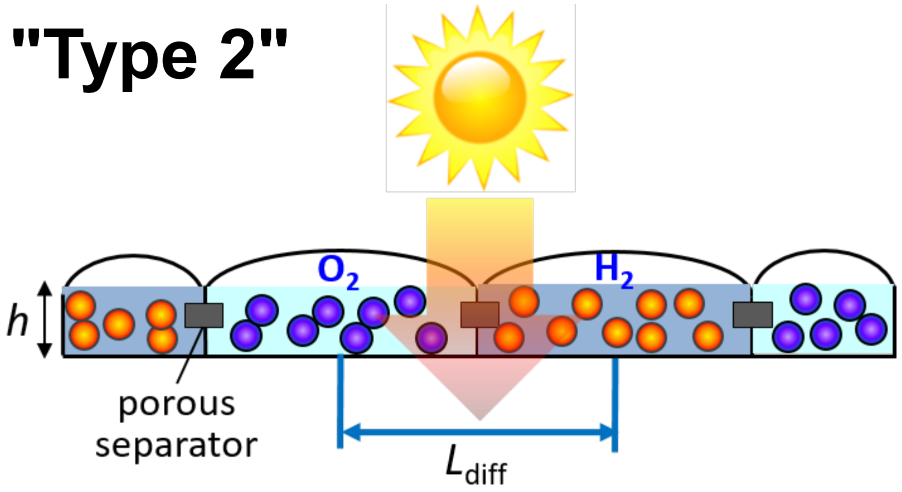
* *The most important and impactful advances over the past year are underlined*

Approach: General Concept

$4.39 at 5%



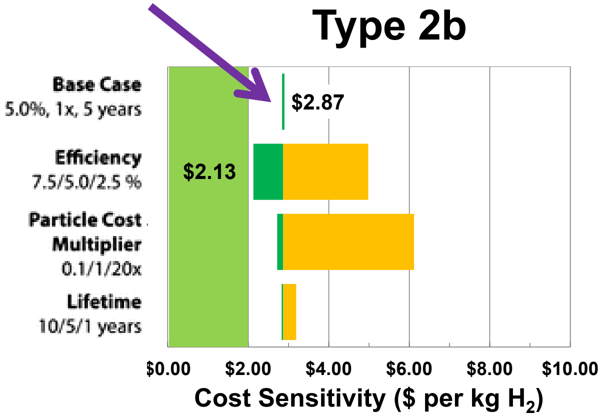
Current "Type 2"

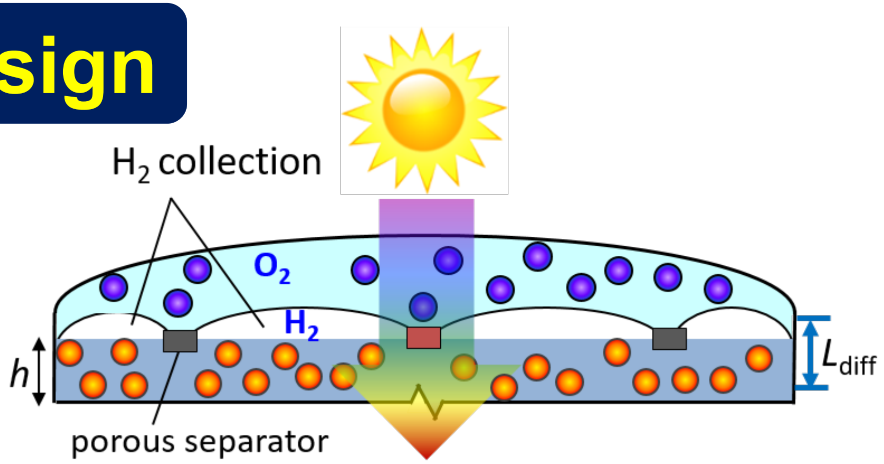


New Stacked-Reactor Design

("Type 2b")

$2.87 at 5%

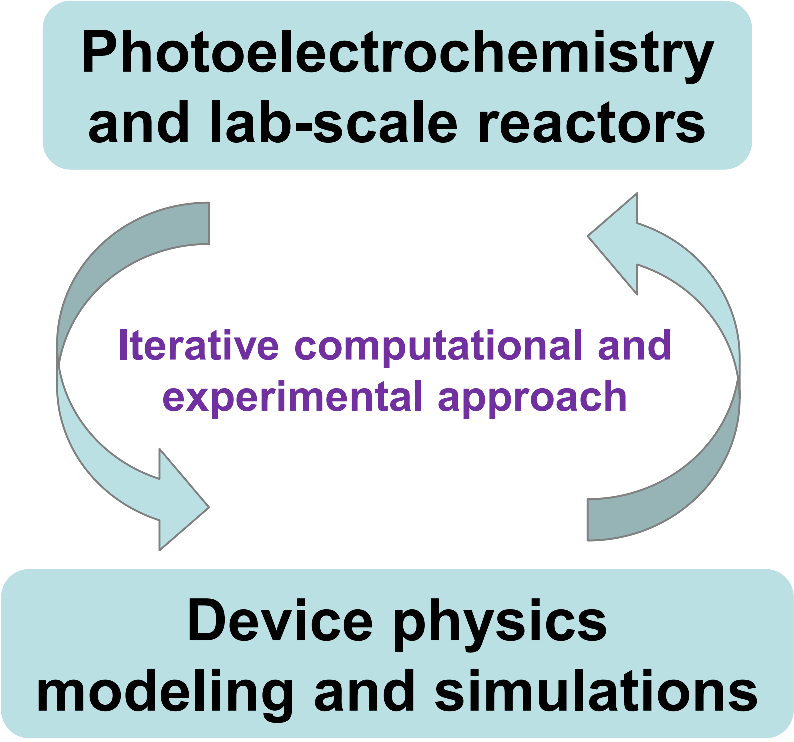




- Serial light absorption increases efficiency
- Much smaller mass transport distances

Directed Technologies, Inc., DOE Report, 2009 & DOE H2A Analysis, https://www.hydrogen.energy.gov/h2a_production.html

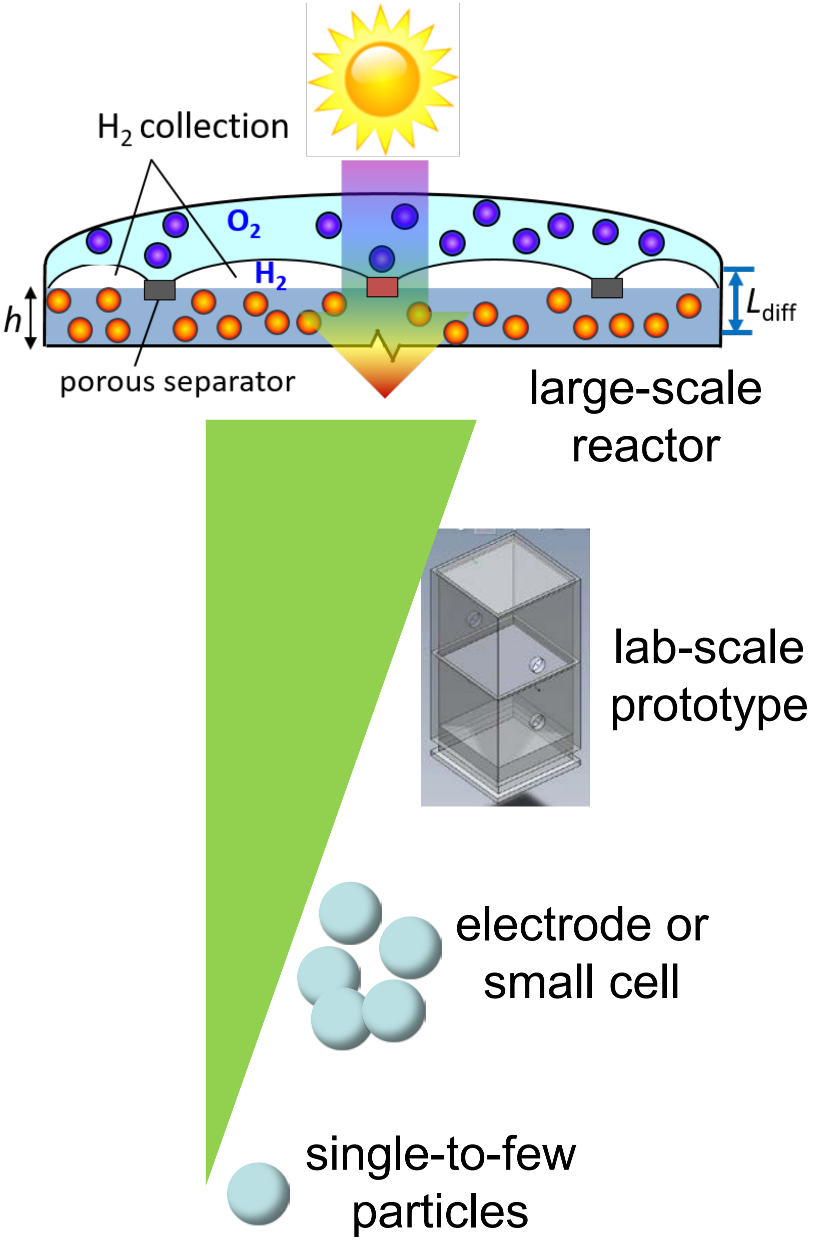
Approach: Overview of RD&D



Photoelectrochemistry and lab-scale reactors

Iterative computational and experimental approach

Device physics modeling and simulations



large-scale reactor

lab-scale prototype

electrode or small cell

single-to-few particles

Approach: R&D Materials Choices

Domen

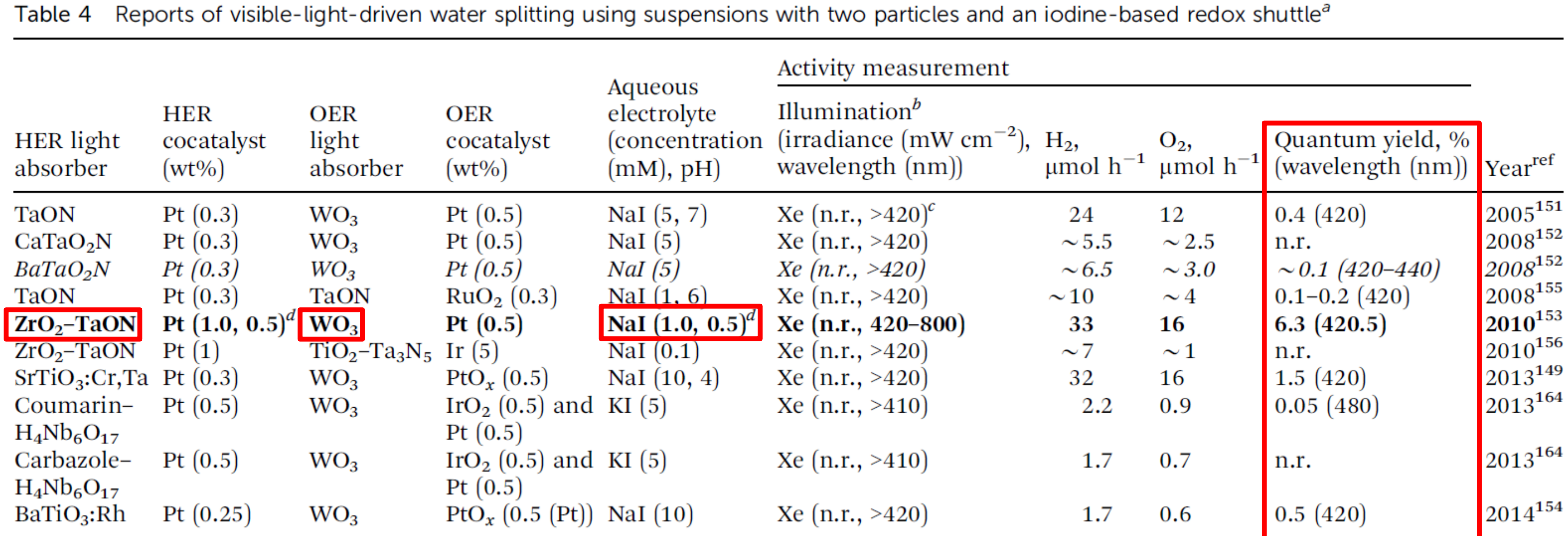


Table 4 Reports of visible-light-driven water splitting using suspensions with two particles and an iodine-based redox shuttle[a]

HER light absorber	HER cocatalyst (wt%)	OER light absorber	OER cocatalyst (wt%)	Aqueous electrolyte (concentration (mM), pH)	Activity measurement: Illumination[b] (irradiance (mW cm^{-2}), wavelength (nm))	H_2, μmol h^{-1}	O_2, μmol h^{-1}	Quantum yield, % (wavelength (nm))	Year$^{\text{ref}}$
TaON	Pt (0.3)	WO_3	Pt (0.5)	NaI (5, 7)	Xe (n.r., >420)[c]	24	12	0.4 (420)	2005[151]
$CaTaO_2N$	Pt (0.3)	WO_3	Pt (0.5)	NaI (5)	Xe (n.r., >420)	~5.5	~2.5	n.r.	2008[152]
$BaTaO_2N$	*Pt (0.3)*	*WO_3*	*Pt (0.5)*	*NaI (5)*	*Xe (n.r., >420)*	*~6.5*	*~3.0*	*~0.1 (420–440)*	*2008*[152]
TaON	Pt (0.3)	TaON	RuO_2 (0.3)	NaI (1, 6)	Xe (n.r., >420)	~10	~4	0.1–0.2 (420)	2008[155]
ZrO_2–TaON	**Pt (1.0, 0.5)**[d]	**WO_3**	**Pt (0.5)**	**NaI (1.0, 0.5)**[d]	**Xe (n.r., 420–800)**	**33**	**16**	**6.3 (420.5)**	**2010**[153]
ZrO_2–TaON	Pt (1)	TiO_2–Ta_3N_5	Ir (5)	NaI (0.1)	Xe (n.r., >420)	~7	~1	n.r.	2010[156]
$SrTiO_3$:Cr,Ta	Pt (0.3)	WO_3	PtO_x (0.5)	NaI (10, 4)	Xe (n.r., >420)	32	16	1.5 (420)	2013[149]
Coumarin–$H_4Nb_6O_{17}$	Pt (0.5)	WO_3	IrO_2 (0.5) and Pt (0.5)	KI (5)	Xe (n.r., >410)	2.2	0.9	0.05 (480)	2013[164]
Carbazole–$H_4Nb_6O_{17}$	Pt (0.5)	WO_3	IrO_2 (0.5) and Pt (0.5)	KI (5)	Xe (n.r., >410)	1.7	0.7	n.r.	2013[164]
$BaTiO_3$:Rh	Pt (0.25)	WO_3	PtO_x (0.5 (Pt))	NaI (10)	Xe (n.r., >420)	1.7	0.6	0.5 (420)	2014[154]

Kudo & Abe & Osterloh

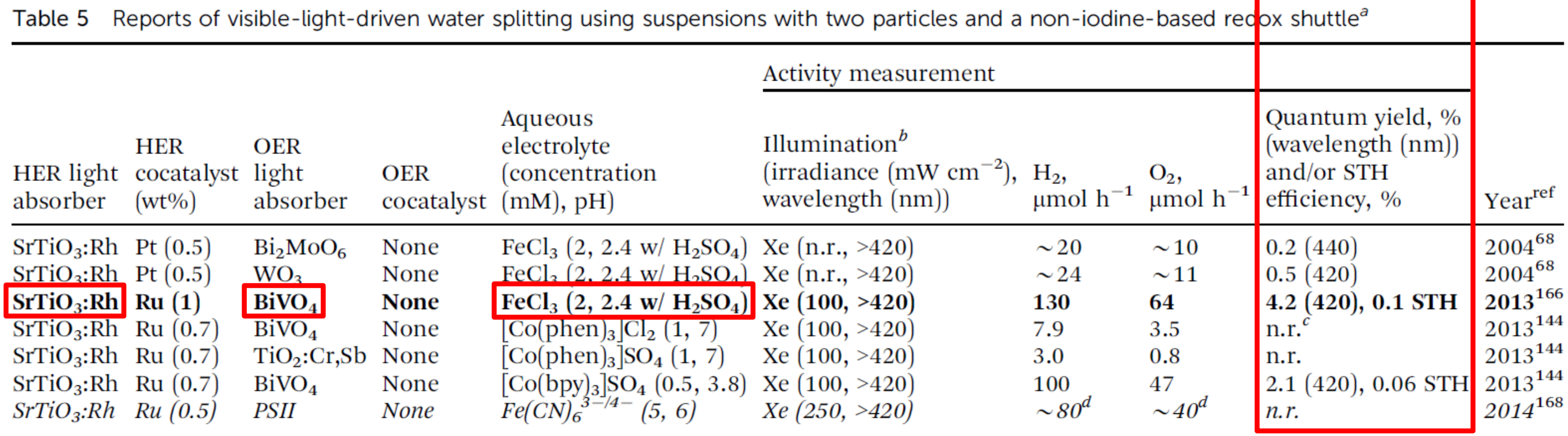


Table 5 Reports of visible-light-driven water splitting using suspensions with two particles and a non-iodine-based redox shuttle[a]

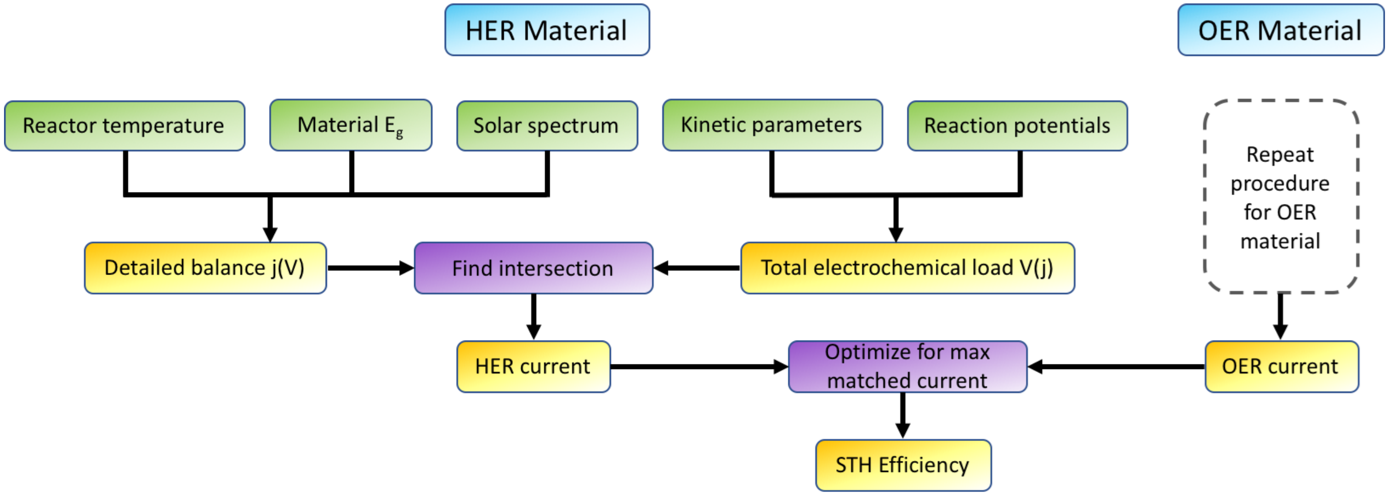
HER light absorber	HER cocatalyst (wt%)	OER light absorber	OER cocatalyst	Aqueous electrolyte (concentration (mM), pH)	Activity measurement: Illumination[b] (irradiance (mW cm^{-2}), wavelength (nm))	H_2, μmol h^{-1}	O_2, μmol h^{-1}	Quantum yield, % (wavelength (nm)) and/or STH efficiency, %	Year$^{\text{ref}}$
$SrTiO_3$:Rh	Pt (0.5)	Bi_2MoO_6	None	$FeCl_3$ (2, 2.4 w/ H_2SO_4)	Xe (n.r., >420)	~20	~10	0.2 (440)	2004[68]
$SrTiO_3$:Rh	Pt (0.5)	WO_3	None	$FeCl_3$ (2, 2.4 w/ H_2SO_4)	Xe (n.r., >420)	~24	~11	0.5 (420)	2004[68]
$SrTiO_3$:Rh	**Ru (1)**	**$BiVO_4$**	**None**	**$FeCl_3$ (2, 2.4 w/ H_2SO_4)**	**Xe (100, >420)**	**130**	**64**	**4.2 (420), 0.1 STH**	**2013**[166]
$SrTiO_3$:Rh	Ru (0.7)	$BiVO_4$	None	$[Co(phen)_3]Cl_2$ (1, 7)	Xe (100, >420)	7.9	3.5	n.r.[c]	2013[144]
$SrTiO_3$:Rh	Ru (0.7)	TiO_2:Cr,Sb	None	$[Co(phen)_3]SO_4$ (1, 7)	Xe (100, >420)	3.0	0.8	n.r.	2013[144]
$SrTiO_3$:Rh	Ru (0.7)	$BiVO_4$	None	$[Co(bpy)_3]SO_4$ (0.5, 3.8)	Xe (100, >420)	100	47	2.1 (420), 0.06 STH	2013[144]
$SrTiO_3$:Rh	*Ru (0.5)*	*PSII*	*None*	*$Fe(CN)_6^{3-/4-}$ (5, 6)*	*Xe (250, >420)*	*~80*[d]	*~40*[d]	*n.r.*	*2014*[168]

Fabian, Hu, Singh, Houle, Hisatomi, Domen, Osterloh & Ardo, *Energy Environ. Sci.*, 2015, *8*, 2825

Approach: Milestones

Description of Milestone	Due Date (Quarter)	Percentage Complete
Task 1.0 Numerical modeling and simulations of new reactor design		
D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH}. **(AH, AI) – in silico, demonstrated sustainable reactors that require no pumps or pipes; reaction conditions could be sustained when operating at a 10% η_{STH} or smaller (See Technical Backup Slides)**	August 1, 2016 (**Q4**)	**100%**
M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow. **(AH, AI) – each of these processes, plus determination of η_{STH} limits, has been implemented, at least in part**	July 1, 2018 ("**Q12" / end**)	90%

Accomplishments: Maximum STH Efficiency



HER Material

OER Material

Reactor temperature

Material E_g

Solar spectrum

Kinetic parameters

Reaction potentials

Repeat procedure for OER material

Detailed balance j(V)

Find intersection

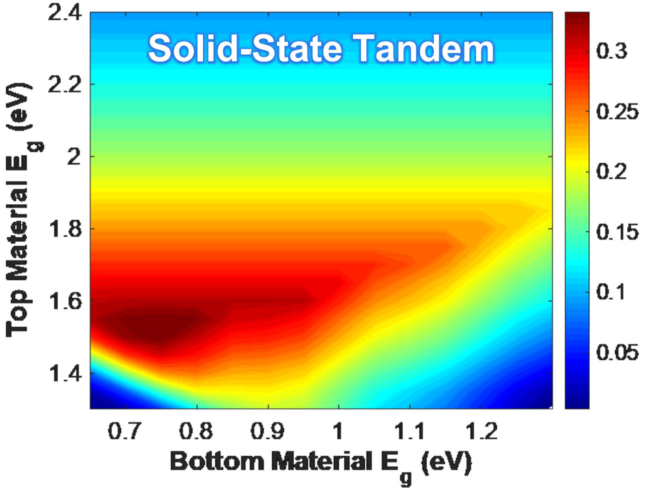
Total electrochemical load V(j)

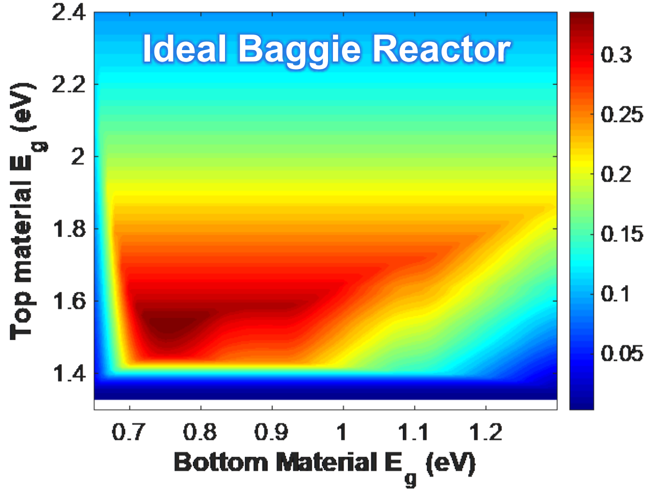
HER current

Optimize for max matched current

OER current

STH Efficiency

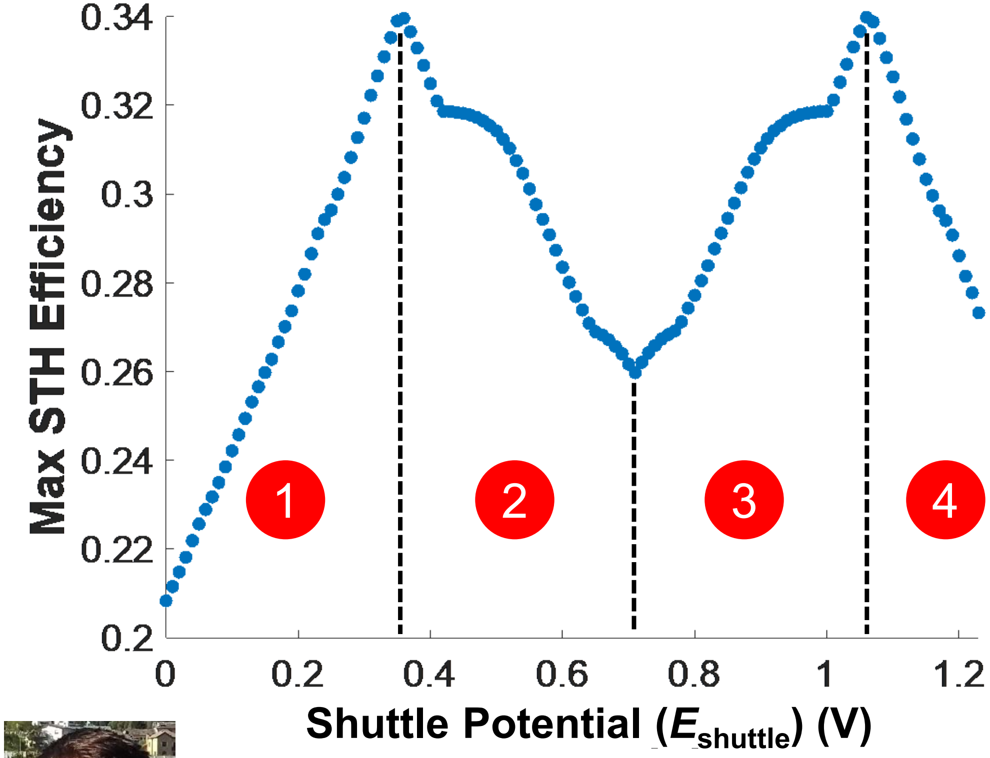




Sam Keene
Physicist
(UCI Ph.D. Student)

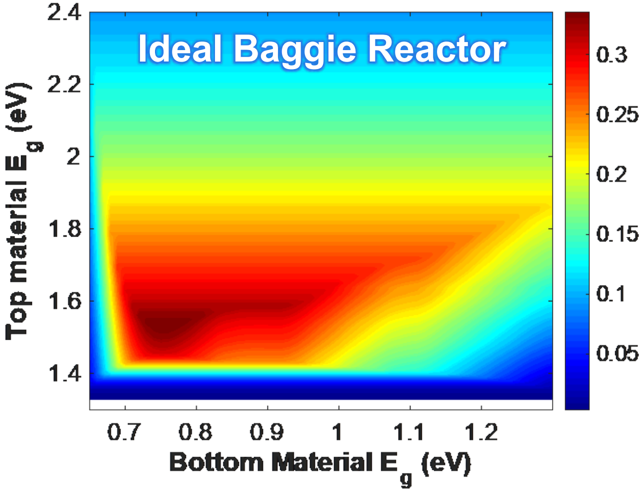
Specific tandem baggie reactors (E_{shuttle} = 0.36 V or 1.06 V *vs* RHE) have the same maximum STH efficiency as a solid-state tandem

Accomplishments: Maximum STH Efficiency



<u>**Maximum STH efficiency limited by light in the top reactor as follows:**</u>

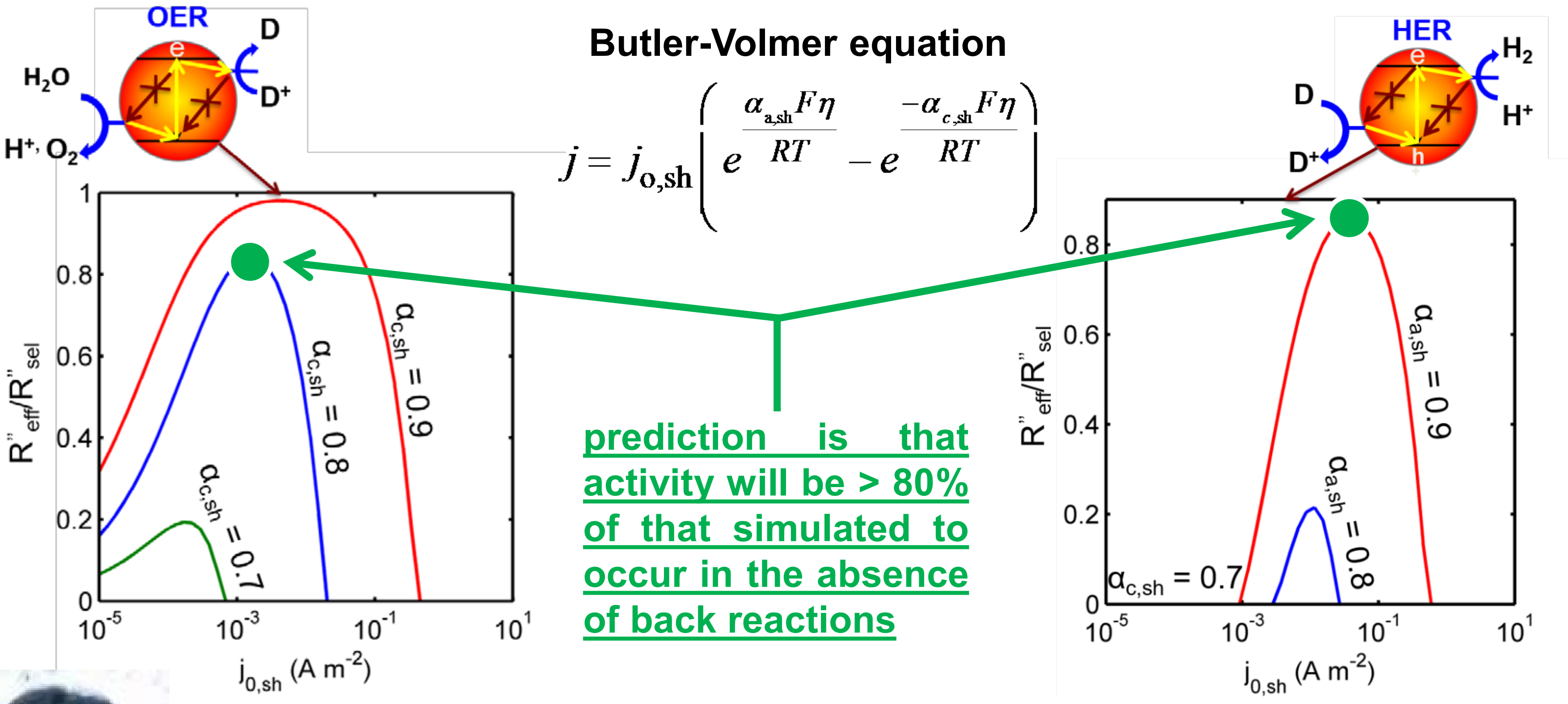
1) Absorption by top OER particles
2) Transmission to bottom HER particles
3) Transmission to bottom OER particles
4) Absorption by top HER particles



<u>Sam Keene</u>
Physicist
(UCI Ph.D. Student)

The maximum possible STH efficiency for any rapid and perfectly selective redox shuttle is > 60% of the global maximum STH efficiency, which is the maximum efficiency for a solid-state tandem

Accomplishments: Back reactions



Butler-Volmer equation

$$j = j_{\mathrm{o,sh}}\left(e^{\frac{\alpha_{\mathrm{a,sh}}F\eta}{RT}} - e^{\frac{-\alpha_{c,\mathrm{sh}}F\eta}{RT}}\right)$$

prediction is that activity will be > 80% of that simulated to occur in the absence of back reactions

Asymmetric redox shuttle electrocatalysis disfavors shunting reactions and will allow for efficient photocatalyst particles

Rohini Bala Chandran
Mechanical Engineer
(LBNL Postdoc;
Asst. Prof. at U. Mich.)

Other Modeling and Simulation Results *(not described in detail on slides elsewhere)*

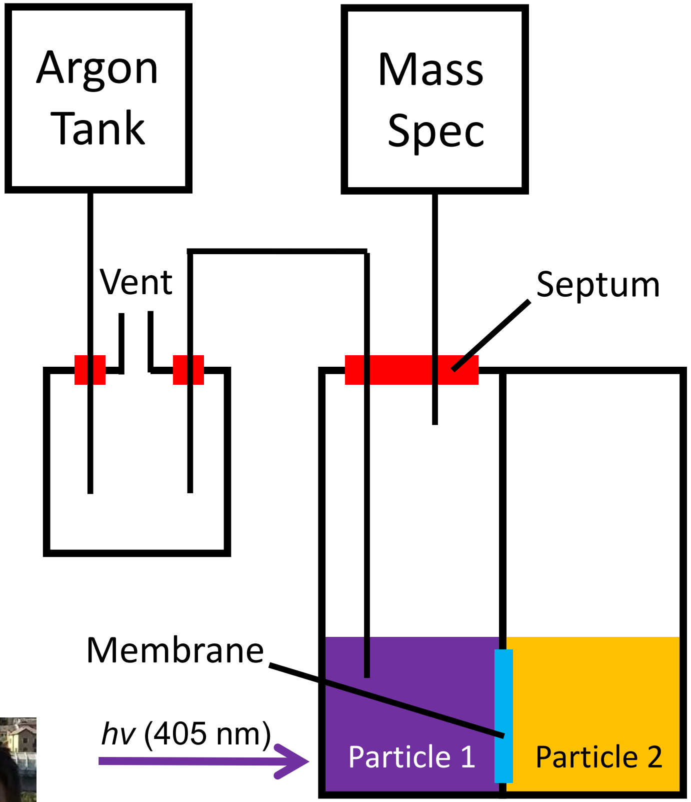
- Transport is more rapid with natural convection due to temperature gradients
- *Models supported by experiments conducted on mixing due to temperature gradients*
- Mie theory for photocatalyst optical effects (Maxwell's equations) is more accurate
- A single-photocatalyst-nanoparticle kinetic model is more accurate than bulk equations

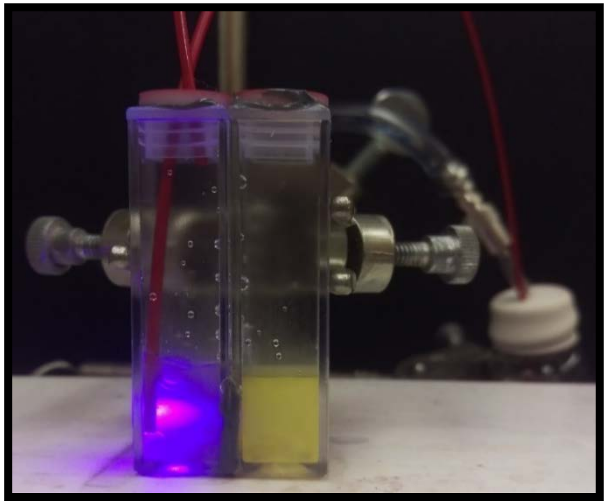
Bala Chandran, Breen, Shao, Ardo & Weber, *Energy Environ. Sci.*, 2018, *11*, 115

Approach: Milestones

Description of Milestone	Due Date (Quarter)	Percentage Complete
Task 1.0 Numerical modeling and simulations of new reactor design		
D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH}. **(AH, AI) – in silico, demonstrated sustainable reactors that require no pumps or pipes; reaction conditions could be sustained when operating at a 10% η_{STH} or smaller (See Technical Backup Slides)**	August 1, 2016 (**Q4**)	**100%**
M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow. **(AH, AI) – each of these processes, plus determination of η_{STH} limits, has been implemented, at least in part**	July 1, 2018 ("**Q12" / end**)	90%
Task 2.0 Experimental evaluation of chemicals, materials, and reactors		
M2.3.2 Demonstrate > 1% η_{STH} in electrode form factor. **(AJ, AG) – 0.1% η_{STH} demonstrated using $Rh:SrTiO_3$ and $BiVO_4$, which was limited by the HER photoelectrode; alternative HER particles, syntheses, and dopants are being explored, with limited success**	May 1, 2017 (**Q7**)	30%
M2.4.1 Demonstrate > 3 L H_2 (and > 1.5 L O_2) from 8 hours of solar illumination. **(AJ, AG, AH, AI) – built and tested model reactors with 10x smaller illumination area than final deliverable; detected H_2 by mass spectrometry during visible-light excitation of a smaller reaction vessel; obtained apparent quantum yields that are consistent with state-of-the-art literature reports**	July 1, 2018 ("**Q12" / end**)	40%

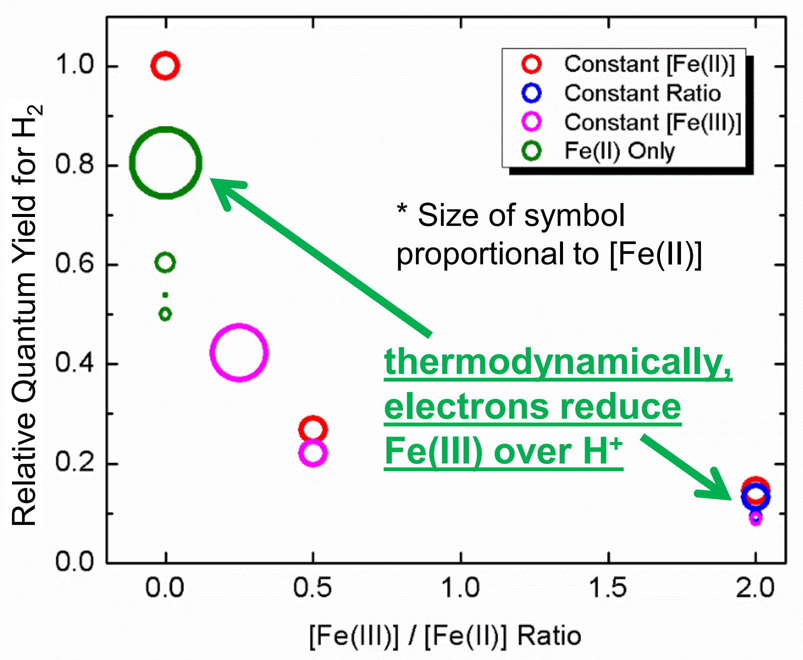
Accomplishments: Rh:SrTiO$_3$ Photocatalysts





Sam Keene
Physicist
(UCI Ph.D. Student)

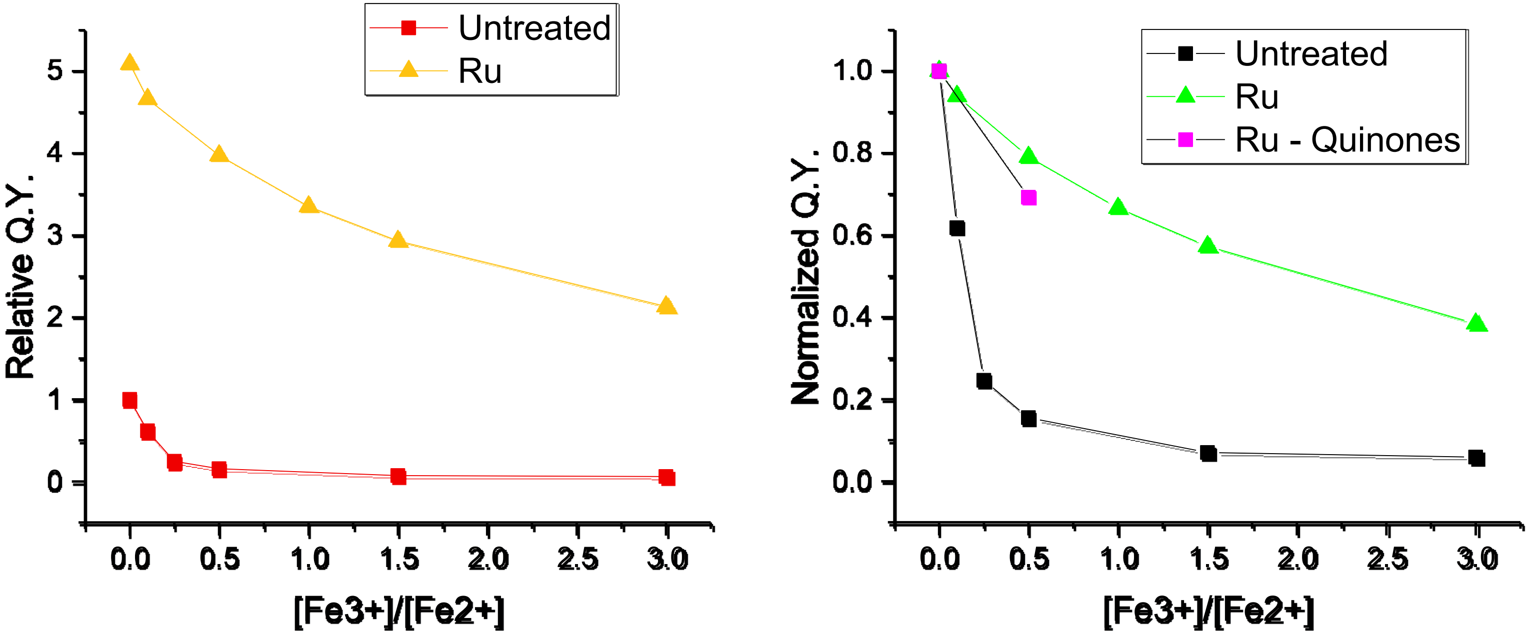
H$_2$ measured from illuminated photocatalysts in 1 cm "tall" reactor containing aqueous Fe(II) redox shuttle



* Size of symbol proportional to [Fe(II)]

thermodynamically, electrons reduce Fe(III) over H$^+$

Accomplishments: Rh:$SrTiO_3$ Photocatalysts



Sam Keene
Physicist
(UCI Ph.D. Student)

Addition of Ru cocatalysts increases quantum yield for H_2 with decreased dependence on [Fe(III)]; hydroquinone is also a good donor

Other Experimental Results *(not described in detail on slides elsewhere)*

- Doped and co-doped $SrTiO_3$ materials were synthesized by various routes
- Low activity for the HER using PEDOT:PSS/$La_5Ti_2CuS_5O_7$ photoelectrodes
- Some electrochemical selectivity by the cocatalysts for the HER/OER

Accomplishments: Quantum Yield Comparisons

Rh:$SrTiO_3$ HER photocatalysts *(405 nm excitation)*

Redox species	no cocatalysts	with Ru cocatalysts	notes *(* all with argon flow)*
methanol *(sacrificial)*	~0%	0.6%	no pH adjustment
Fe(II)	**0.3%**	**1.0%**	**same response at pH 1 – 2.4; no response at high pH**
hydroquinone	~0%	0.09%	no pH adjustment; reducing pH had no effect
iodide	0%	0%	pH 7 and 11 investigated

Conditions	cocatalyst type	rate of H_2 Production (μmol h^{-1})	quantum yield
reduced pressure	Pt	1.3, with methanol *(sacrificial)*	0.7%
nitrogen flow	Pt	3.7, with methanol *(sacrificial)*	2.1%
argon flow	Pt	4.4, with methanol *(sacrificial)*	2.4%
reduced pressure	Ru	2.0, with methanol *(sacrificial)*	1.1%

Mo:$BiVO_4$ OER photocatalysts *(405 nm excitation)*

Redox species	without cocatalysts	notes *(* all with argon flow)*
Ag(I) *(sacrificial)*	2.6%	no pH adjustment
Fe(III)	**1.5%**	**pH 2**
quinone	0	no pH adjustment
IO_3^-	0	pH 7 and 11 investigated

Sam Keene
Physicist
(UCI Ph.D. Student)

William Gaieck
Materials Scientist
(UCI Ph.D. Student)

Similar Q.Y. for OER (Mo:$BiVO_4$) and HER (Rh:$SrTiO_3$)

Response to previous year reviewers' comments

"When measured toward Hydrogen and Fuel Cells Program goals, the project is an order of magnitude away, and it is difficult to see a pathway for it to achieve overall goals." / "The project might drop the three-liter demonstration if it is a large distraction."

This project aimed to realize an increase in the STH efficiency of photocatalyst reactors using several new approaches. These approaches were not very successful and were further hampered by poor materials performance. Therefore, the focus in the final months of the project has shifted away from the 3 SLH_2 demonstration, and instead on understanding photocatalyst reactivity and disseminating this to the community. This project was funded under an Incubator FOA and so it was intended to be slightly higher risk.

"The researchers want to achieve a cost target of \$20/kg H_2 while achieving a 1% solar efficiency. Put another way, if they somehow miraculously achieved 20% efficiency, their costs would be \$1/kg H_2." / "Regarding modeling, the project might consider generating theoretical STH iso-contour plots with E_{g1} and E_{g2} on the x- and y-axes".

A techno-economic analysis using the H2A tool was conducted and it suggests that this new design is cost-effective. (The efficiency and cost do not scale linearly.) Results from our STH efficiency models were unexpected and will help guide future research.

"It is clearly time to put real particle suspensions in the baggie and see what happens. It would be best if they can find time to develop a model of the nanoparticles before they start fabricating them." / "What is really needed is better [PEC] materials".

For nearly one year, we have been measuring the STH efficiency from particle suspensions. The quantum yields are as expected based on the literature. A device physics model is currently under development for single particle photochemistry, but it is still incomplete.

Collaborations

Primary team members *(funded)*

- Lawrence Berkeley National Laboratory (Federal Lab) & Joint Center for Artificial Photosynthesis (DOE Hub)
  - **Adam Weber (sub-recipient; part of HydroGEN)**: Core numerical device-multi-physics modeling and simulation effort with unique expertise in coupled transport phenomena
- California Institute of Technology (University) & Joint Center for Artificial Photosynthesis (DOE Hub)
  - **Chengxiang Xiang (sub-contracted advisor; part of HydroGEN)**: Unique expertise in numerical device-multi-physics modeling and simulation of related photoelectrochemical devices

Additional team members with materials synthesis expertise *(unfunded)*

- Tokyo University of Science, **Akihiko Kudo ($Rh:SrTiO_3$, $BiVO_4$)**

Remaining Challenges and Barriers

Task 1.0 Numerical modeling and simulation of new reactor design

- Complete analyses for STH efficiency dependence on bandgap energies and potential of the redox shuttle.
- Complete complex fluid flow model to enable simulation of convection, e.g. pumping/mixing, thermal effects.
- Complete advanced optical phenomena model to more accurately model E&M and particle photophysics.
- Complete more accurate model for photocatalyst reactivity by modeling individual reactions on particles instead of baggie ensemble behavior as an ideal diode coupled to empirical Butler–Volmer electrokinetics.

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

- Complete photocatalyst performance measurements and perform several parametric studies.
- Complete studies on selective electrocatalysis at electrodes for the HER/OER versus redox shuttle reactions.
- Complete analyses of temperature gradient effects on natural convection in prototypes.
- Observe redox shuttle concentrations in a prototype reactor that are consistent with numerical simulations under simulated day–night cycling as an indicator of the accuracy of the device physics models.
- Identify material(s) that operate at a rate consistent with > 1% η_{STH} in electrode form factor and as particle suspensions, as prerequisites to the original final deliverable of > 3 SLH_2 from 8 hours of solar illumination.

Any proposed future work is subject to change based on funding levels.

Proposed Future Work

Project Objective: **Experimentally validate** a *new design* for scalable solar-H_2 technologies using laboratory-scale prototype particle suspension reactors

Description of Milestone – Solution	Due Date (Quarter)	Percentage Complete
Task 1.0 Numerical modeling and simulation of new reactor design		
M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow – **Introduce these phenomena into the master modeling framework and validate results from the simulations; also determine the efficiency limits of these types of reactors as a function of redox shuttle**	July 1, 2018 ("**Q12" / end**)	90%
Task 2.0 Experimental evaluation of chemicals, materials, and reactors		
M2.3.2 Demonstrate > 1% η_{STH} in electrode form factor **– Using efficient thin-film and mesoporous electrodes with photochemically deposited electrocatalysts, optimize conditions**	May 1, 2017 (**Q7**)	30%
M2.4.1 Demonstrate > 3 standard L of H_2 (and > 1.5 L of O_2) from 8 hours of solar illumination **– Using electrodes and free-floating particles, continue to assess the impacts that redox shuttles have on the rate of H_2 evolution; introduce selective catalysis through interfacial engineering of light absorbers and catalysts; combine particles, prototype reactors, and redox shuttles and measure rates of H_2 evolution under solar illumination**	July 1, 2018 ("**Q12" / end**)	40%

Any proposed future work
is subject to change
based on funding level

**** Additional funding to support follow-on work has not yet been obtained***

Project Summary

Project Objective: **Experimentally validate** a *new design* for scalable solar-H_2 technologies using laboratory-scale prototype particle suspension reactors

Relevance	Techno-economic analyses of particle suspension reactors with side-by-side compartments suggest that H_2 cost may be rather inexpensive.
Approach	Stack the compartments to realize the tandem efficiency advantage and shorten the mass transport distance so that fewer pumps and pipes are required to circulate the electrolyte.
Technical Accomplishments	Using a validated device physics model, we numerically demonstrated stable operation of a tandem reactor operating at up to a 10% STH efficiency and assuming most relevant physics. We also synthesized and characterized efficient photoelectrodes consisting of Rh-modified $SrTiO_3$, WO_3, or $BiVO_4$ and for each of these, demonstrated photocurrents at a rate consistent with a 1% STH efficiency. We also developed prototype reactors and techniques to locally assess redox shuttle concentration *in situ*. **We also demonstrated state-of-the-art quantum yields from our materials as nanoparticle suspensions.**
Collaborations	*Weber* / *Xiang* for numerical modeling; *Kudo* for materials synthesis.
Proposed Future Work	Add additional device physics to the numerical models and synthesize high quality metal-oxide particles that attain a large quantum yield.

Technical Backup Slides

Relevance: Motivation

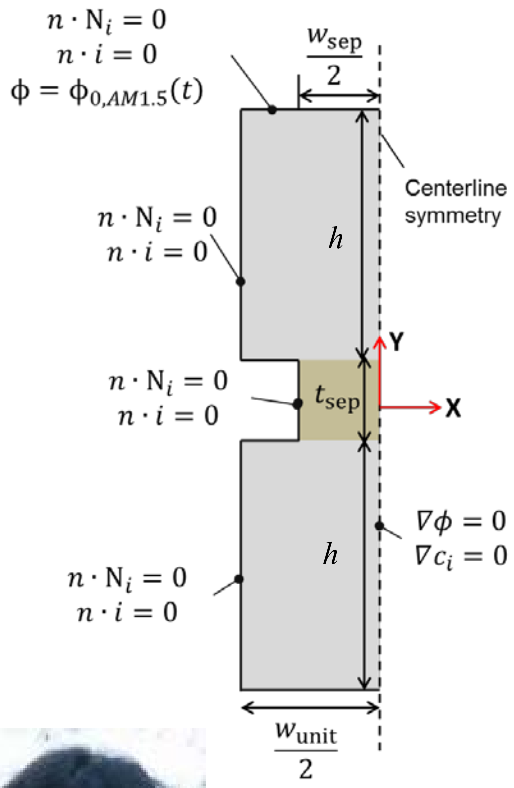
Table 5 Summary of all direct capital expenditures and installation costs for the four different 1 TPD net H_2 production plant modules

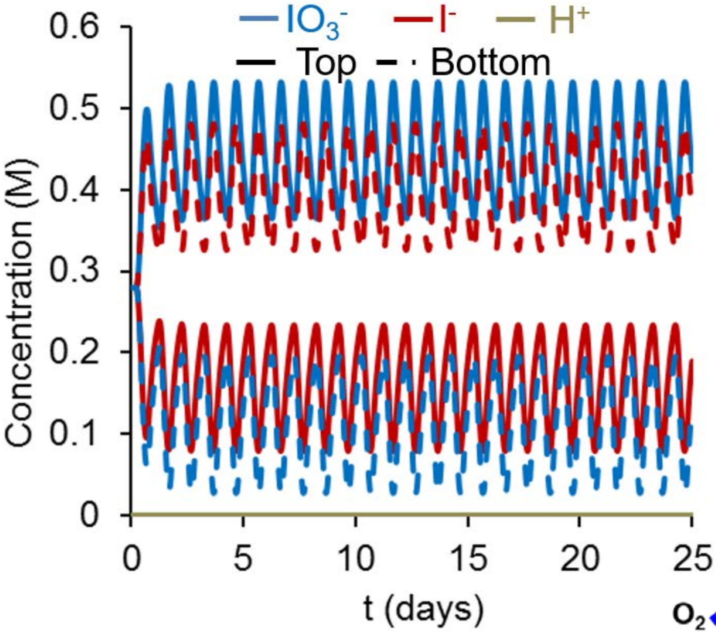
	Type 1, single bed particle suspension		Type 2, dual bed particle suspension		Type 3, fixed panel array		Type 4, tracking concentrator array	
Reactor subassembly	Baggies	$133 077	Baggies	$791 250			Tracking/ concentrating	$2 035 420
	Particles	$22 679	Particles	$40 798	PEC cells	$8 238 271	PEC cells	$1 072 904
	Other	$56 501	Other	$60 886	Other	$105 074	Other	$26 886
Reactor subassembly total	$212 257		$892 934		$8 343 345		$3 135 209	
Gas processing subassembly	Compressor	$526 302						
	Condenser	$13 765	Compressor	$315 884	Compressor	$759 481		
	Intercoolers	$30 655	Condenser	$10 626	Condenser	$16 607	Condenser	$7098
	PSA	$107 147	Intercoolers	$23 334	Intercoolers	$36 389	Piping	$26 673
	Piping	$6416	Piping	$6811	Piping	$104 861		
Gas processing subassembly total	$684 283		$356 654		$917 338		$33 771	
Control system total	$173 944		$440 826		$319 862		$279 774	
Direct capital cost total	$1 070 485		$1 690 414		$9 580 545		$3 448 755	
Reactor cost per capture area (uninstalled)	$2.21 per m^2		$6.55 per m^2		$154.95 per m^2		$92.41 per m^2	
System Cost per capture area (uninstalled)	$19.76 per m^2		$18.46 per m^2		$204.81 per m^2		$126.51 per m^2	
Installation	Excavation	$46 259	Excavation	$124 672	Panels/reactor	$1 076 962	Reactors	$746 385
	Baggies/piping	$21 534	Baggies/piping	$291 441	Piping	$30 843	Piping	$10 521
	Gas processing	$203 361	Gas processing	$104 953	Gas processing	$243 743	Gas processing	$2129
	Control system	$52 183	Control system	$132 248	Control system	$95 959	Control system	$83 932
Installation cost total	$323 337		$653 314		$1 447 507		$842 967	
Total capital cost with installation	$1 393 822		$2 343 728		$11 028 052		$4 291 722	

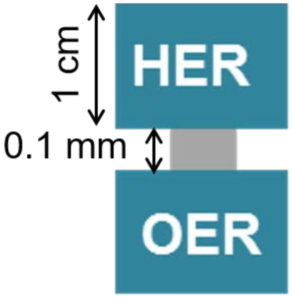
← Half of this cost is due to PVC pipes & pumps

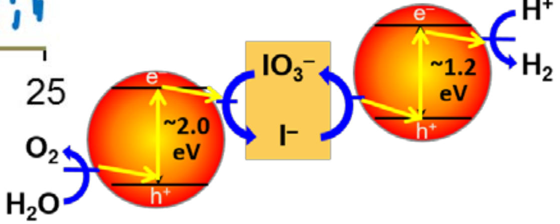
Directed Technologies, Inc., DOE Report, 2009 & Pinaud, …, Ardo, …, Jaramillo, *Energy Environ. Sci.*, 2013, *6*, 1983
DOE–EERE, H2A Analysis, http://www.hydrogen.energy.gov/h2a_production.html

Prior Accomplishments: 10% STH Model







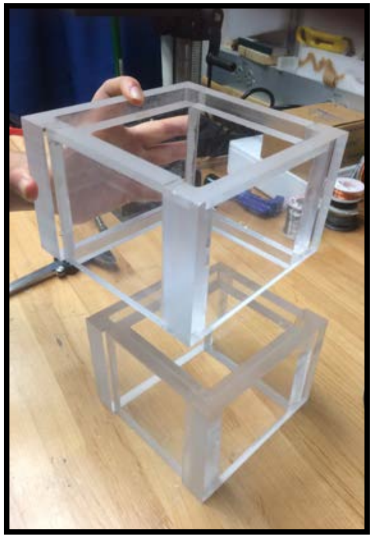


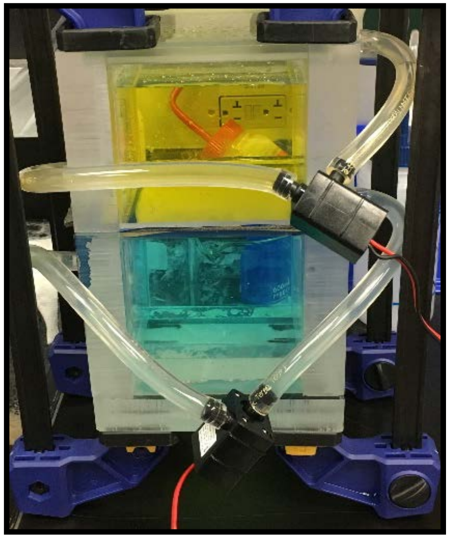
Rohini Bala Chandran
Mechanical Engineer
(LBNL Postdoc;
Asst. Prof. at U. Mich.)

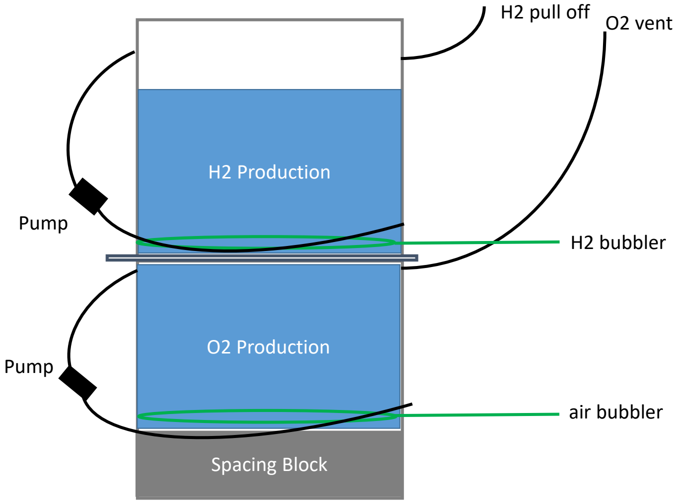
Steady-periodic conditions for **10% STH efficiency** with zero convection (indefinite operation)

- Beer's Law for optimal light absorber photodiodes
- State-of-the-art electrocatalysis & Butler–Volmer parameters
- Light absorption by IO_3^-/I^- redox shuttle within solubility limits
- Redox shuttle transport governed by diffusion and drift
- Non-H^+ counterion for redox shuttle (adjustable pH)
- Separator thickness and porosity limit H_2/O_2 crossover

Prior Accomplishments: Lab Prototypes

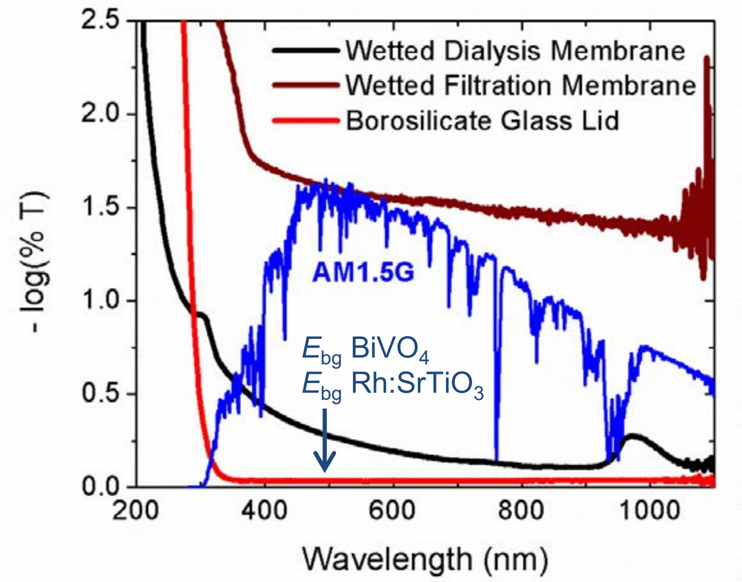




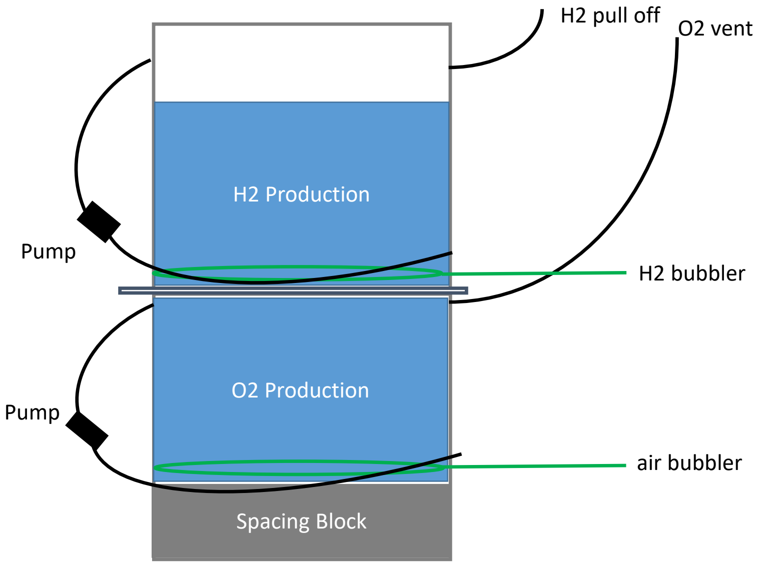


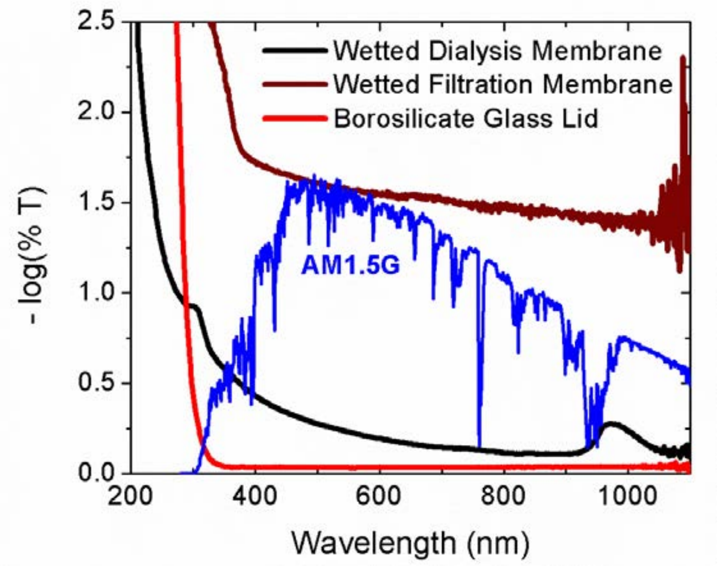
Separators assessed in leak-free Plexiglas prototype reactor (4 x 4 x 8”)

Kevin Tkacz
Materials Scientist
(UCI Ph.D. Student)



Prior Accomplishments: Separators





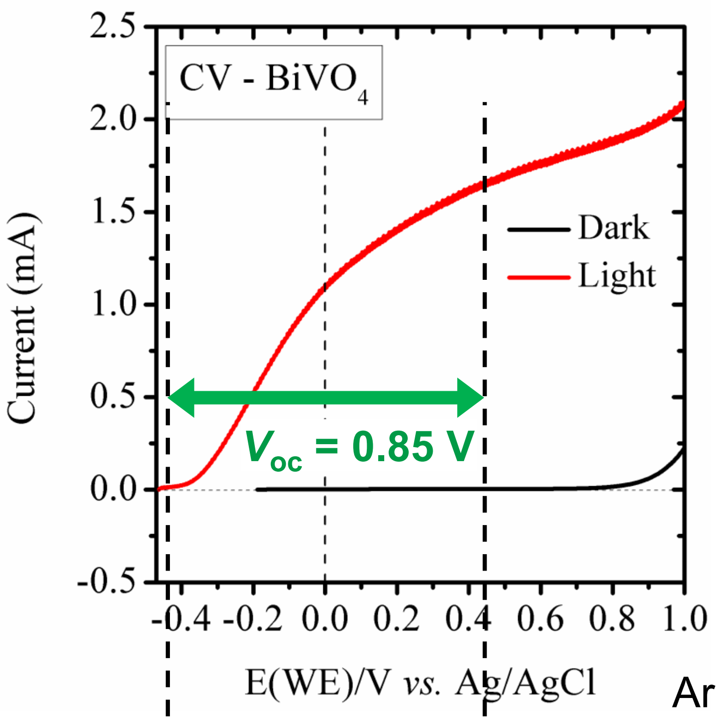
Kevin Tkacz
Materials Scientist
(UCI Ph.D. Student)

	Dialysis Membrane	Snyder ultrafiltration Membrane	Genpore Plastic	Polyvinyl Membrane
Transparent	🟩	Opaque	Opaque	🟩
Dye Diffusion	Slow	🟩	No diffusion	🟩
NP diffusion	Some leakage	–	–	Macroscopic Holes
Physically Robust	🟩	🟩	🟩	Fell apart

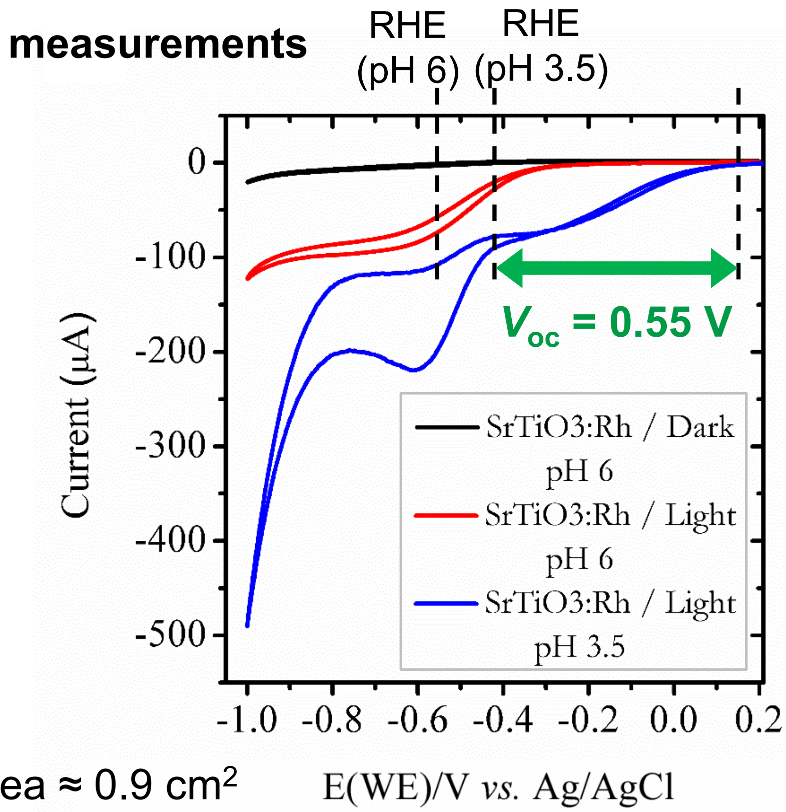
A suitable nanoporous separator has not been identified

Prior Accomplishments: PEC Electrodes

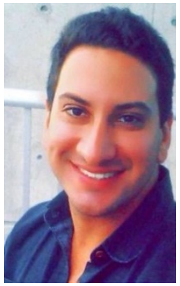
3-electrode measurements



RHE (pH 10) + 1.23 V



Area ≈ 0.9 cm^2



Houman Yaghoubi
Electrical Engineer
(UCI Postdoc; Senior Scientist at Genalyte)

Rh-modified $SrTiO_3$ and $BiVO_4$ can generate > 1.23 V, but efficiency is limited by Rh:$SrTiO_3$ $J \approx 0.1$ mA cm^{-2}