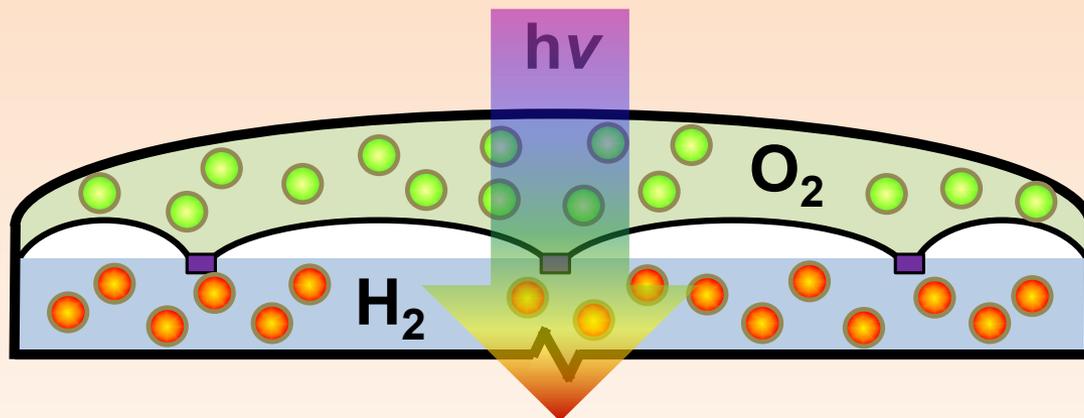


Tandem particle-slurry batch reactors for solar water splitting

Shane Ardo

University of California, Irvine



This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Project Timeline

- Start date: August 1, 2015
- End date: July 31, 2017
(24-month period of performance)

Budget

- Project funding: \$1,248,063
 - Federal funds: \$ 993,759
 - UCI cost share: \$ 254,304
- Funding by year
 - Year 1 spent (2/29): \$ 378,347
 - Year 1 budget: \$ 685,210

Barriers Addressed

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

Partners / Collaborators

- Device-physics modeling & simulation contributors
 - **Lawrence Berkeley National Laboratory & JCAP** (Adam Weber, *sub-recipient*)
 - **California Institute of Technology & JCAP** (Chengxiang Xiang, *sub-contracted advisor*)
- Materials Contributors
 - **Kyoto University** (Ryu Abe)
 - **Tokyo University of Science** (Akihiko Kudo)
 - **University of California, Davis** (Frank Osterloh)
 - **University of California, Riverside** (Phil Christopher)
 - **University of Houston** (Jiming Bao)
 - **University of Tokyo** (Kazunari Domen)



Relevance

Project Objective: **Experimentally validate** a laboratory-scale particle suspension reactor as a scalable technology for solar H₂ production

2015–2016 Objective: **Numerically demonstrate** the feasibility of a reactor that exhibits 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 |

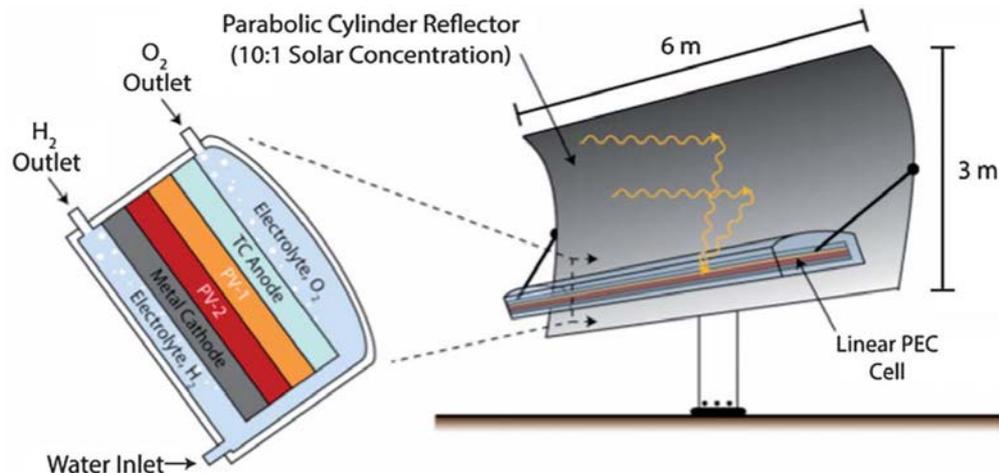
| DOE Barriers | Project Goal |
|---|--|
| (AG) Integrated Device Configurations (AJ) Synthesis and Manufacturing | <ul style="list-style-type: none"> Electrodeposit catalysts on light-absorber particles using bipolar electrochemistry and photoelectrodeposition |
| (AH) Reactor Designs | <ul style="list-style-type: none"> Numerically model and simulate new designs for tandem two-compartment particle suspension reactors Fabricate and evaluate model reactors, and assess their transport capabilities |
| (AI) Auxiliary Materials | <ul style="list-style-type: none"> Identify the most efficient redox shuttles based on rates of mass transport and rates of electrocatalysis at carbon |

Relevance

Wafers (Type 4) and Particles (Type 2)

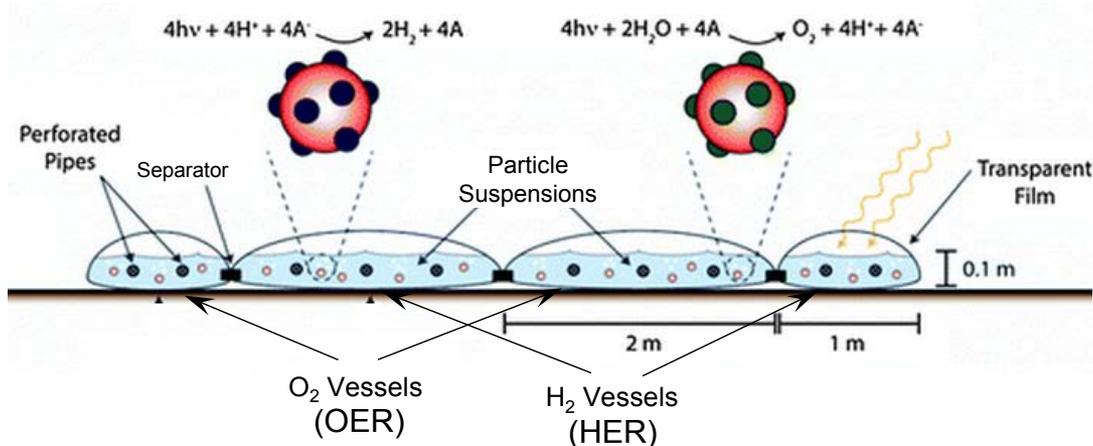
Wafer-based Design

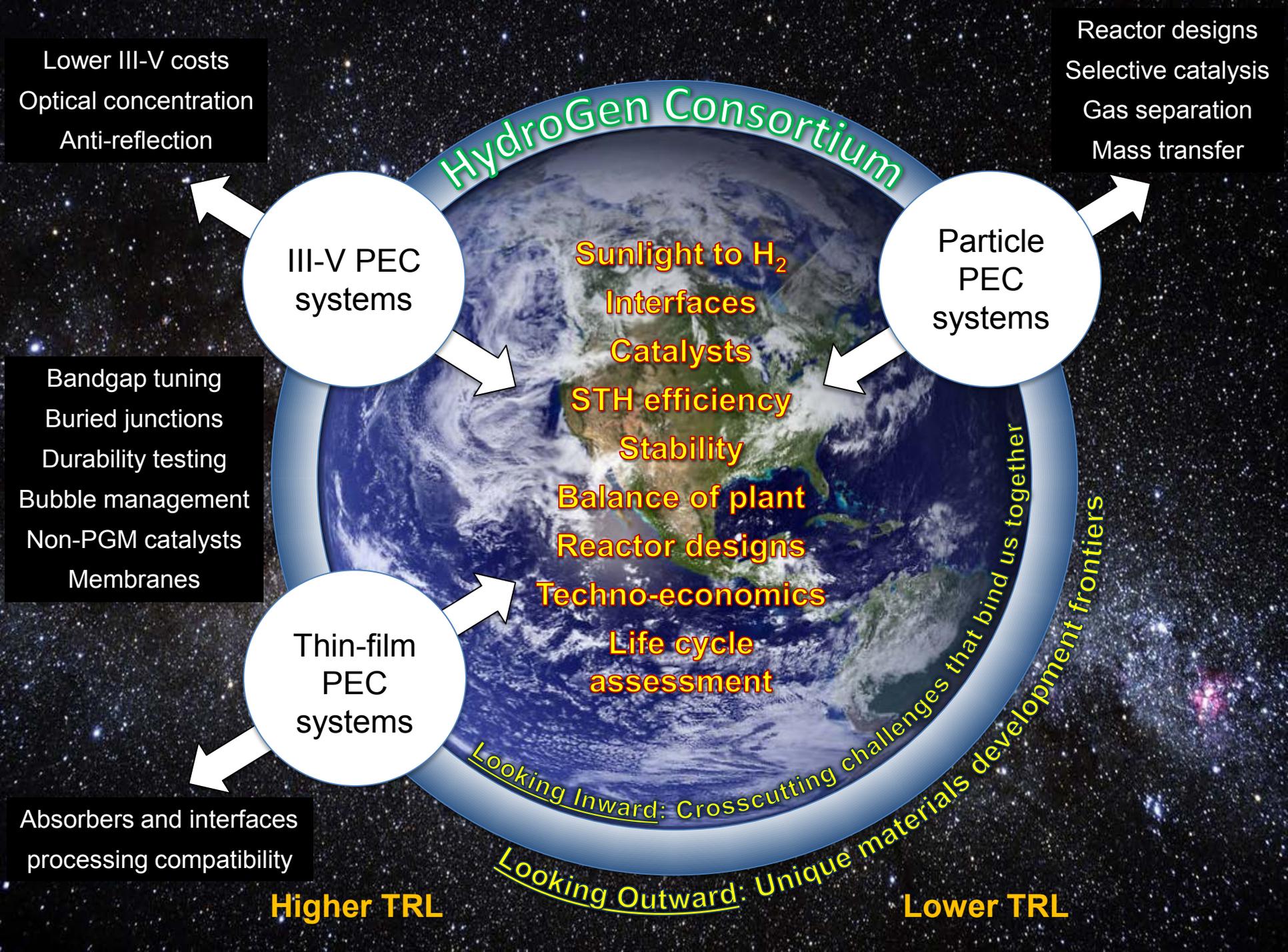
Photoelectrodes immersed in electrolyte and illuminated with an optical concentration of 10x or more



Particle-based Design

Solar water splitting reactor consisting of two particle suspensions arranged side-by-side and connected by a porous via to allow mixing of the molecular redox shuttle (A/A^-).





HydroGen Consortium

III-V PEC systems

- Lower III-V costs
- Optical concentration
- Anti-reflection

Particle PEC systems

- Reactor designs
- Selective catalysis
- Gas separation
- Mass transfer

Thin-film PEC systems

- Bandgap tuning
- Buried junctions
- Durability testing
- Bubble management
- Non-PGM catalysts
- Membranes

- Absorbers and interfaces
- processing compatibility

- Sunlight to H₂
- Interfaces
- Catalysts
- STH efficiency
- Stability
- Balance of plant
- Reactor designs
- Techno-economics
- Life cycle assessment

Looking Inward: Crosscutting challenges that bind us together

Looking Outward: Unique materials development frontiers

Higher TRL

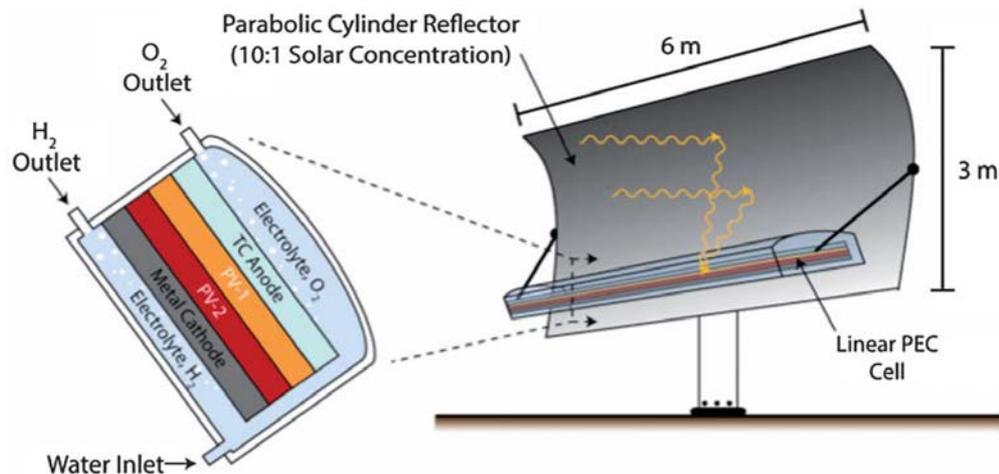
Lower TRL

Relevance

Wafers (Type 4) and Particles (Type 2)

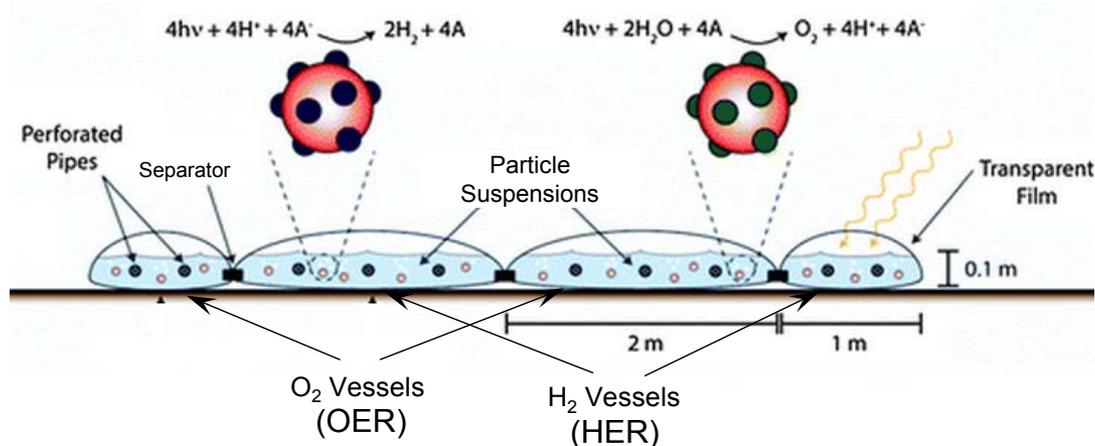
Wafer-based Design

Efficient and high-quality III-V materials with decades of prior R&D, well-understood materials properties, and often incorporated in standard device architectures with light-absorbing layers integrated with electrocatalysts



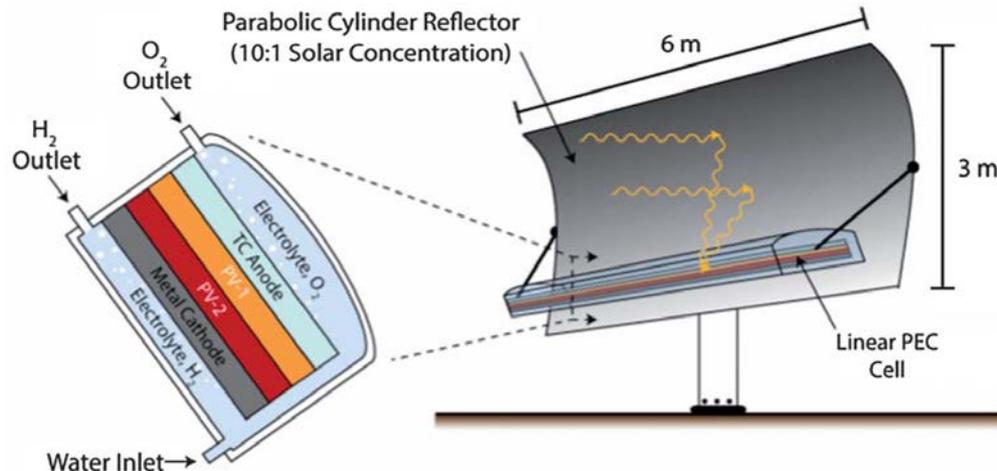
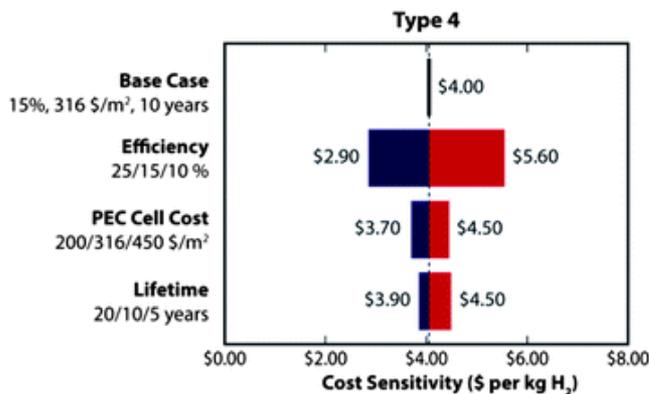
Particle-based Design

High-surface-area materials with low state-of-the-art efficiencies (as reported by only a few research groups) but with flexibility in reactor architecture due to free-floating light absorbers

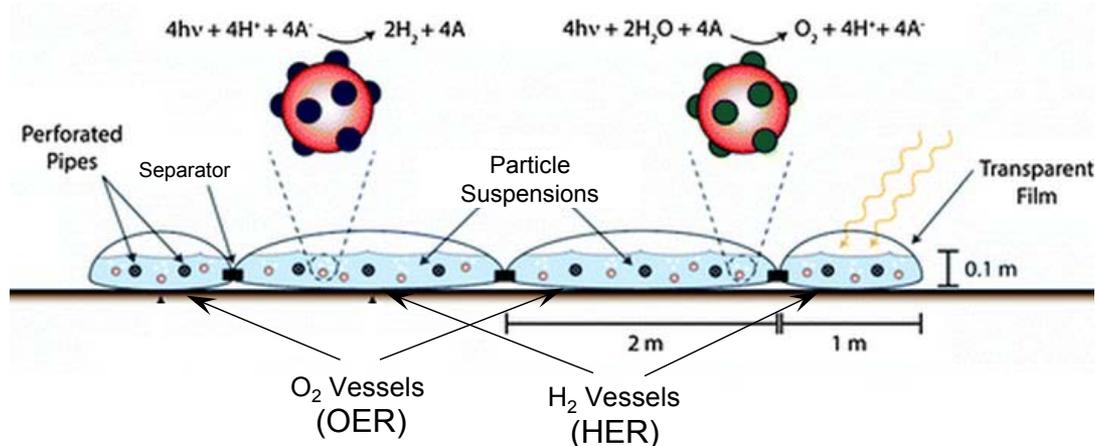
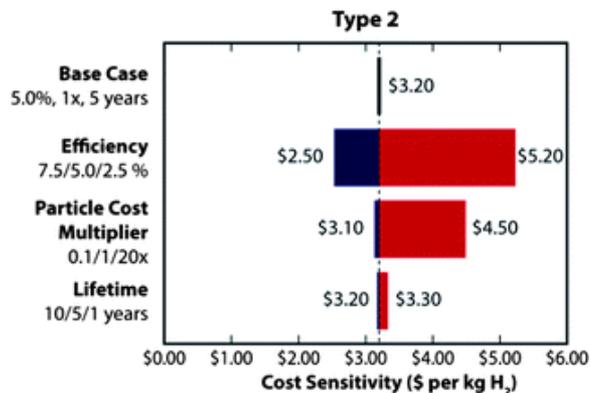


Relevance

Wafers (Type 4) and Particles (Type 2)



DOE Ultimate Target: \$2.10/gge H₂



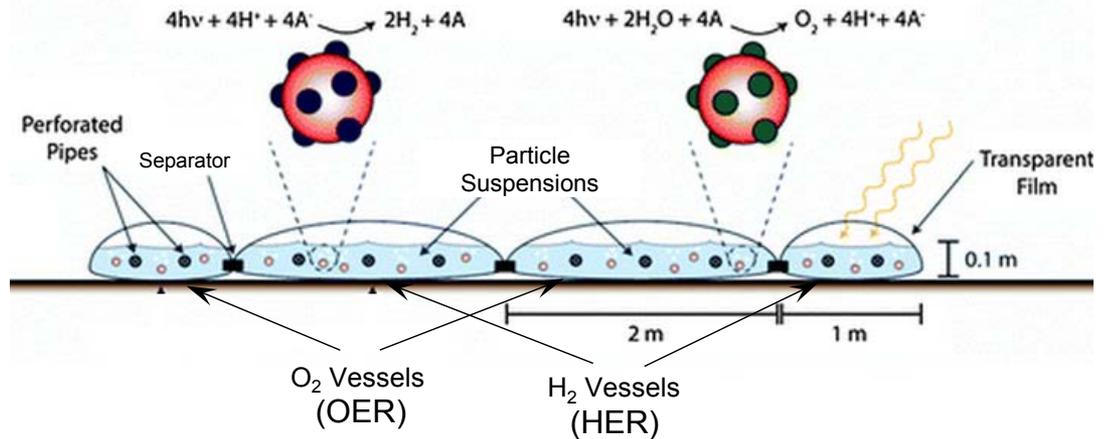
Approach: Concept

New Type 2 Reactor Design

Conventional Design

Solar water splitting reactor consisting of two particle suspensions arranged side-by-side and connected by a porous via to allow mixing of the molecular redox shuttle (A/A^-).

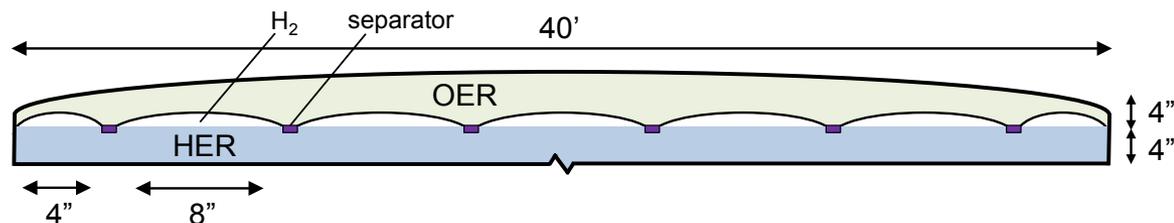
Limitation: Large mass transport distances for A/A^- and no η_{STH} benefit for the tandem design.



New Design

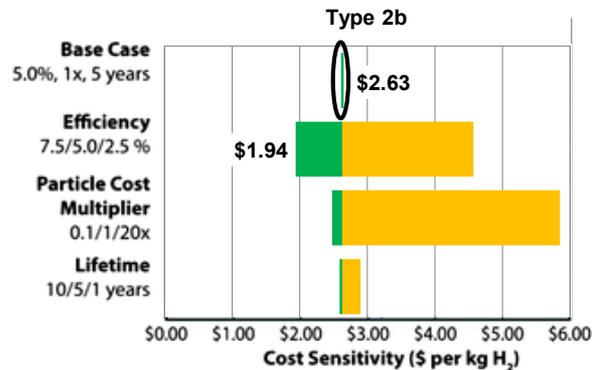
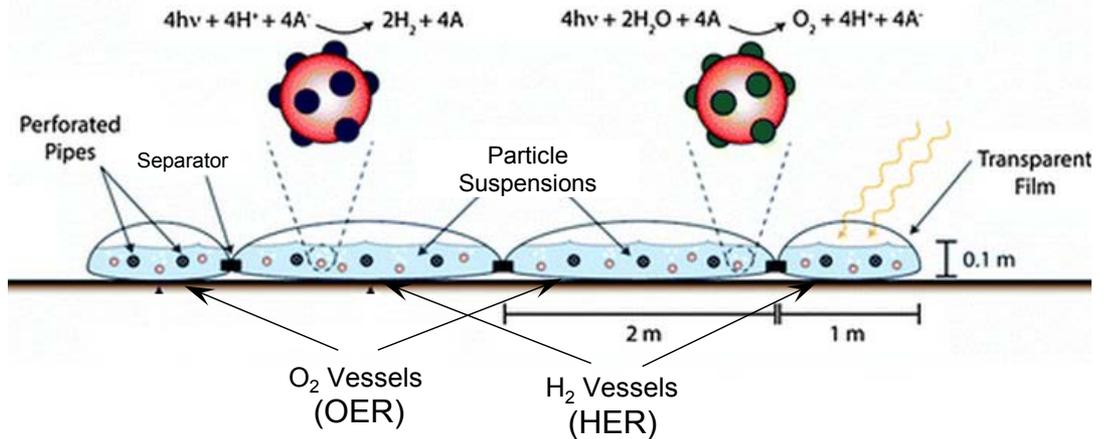
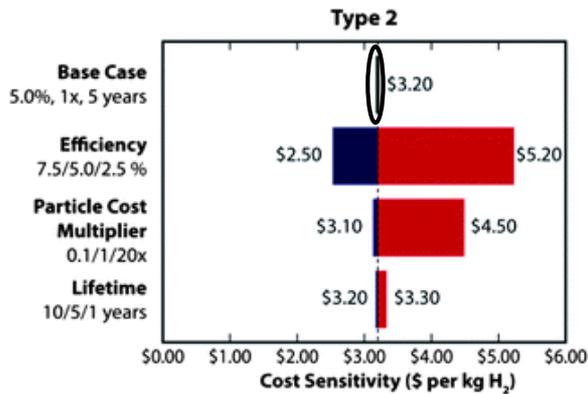
Stacked vessels afford:

- Small transport distances
- ~50% increase in maximum theoretical STH conversion efficiency
- Reduced PVC piping & pumps

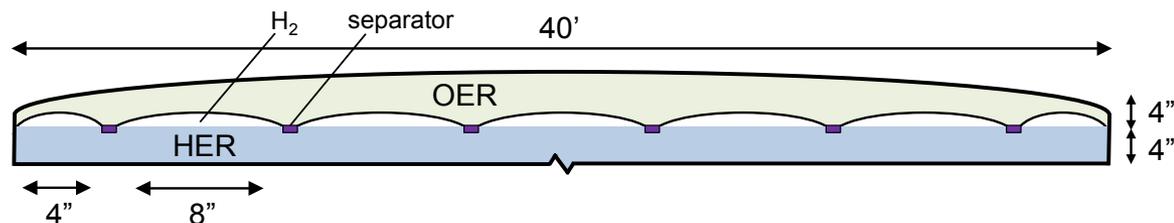


Approach: Concept

New Type 2 Reactor Design



| 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 |



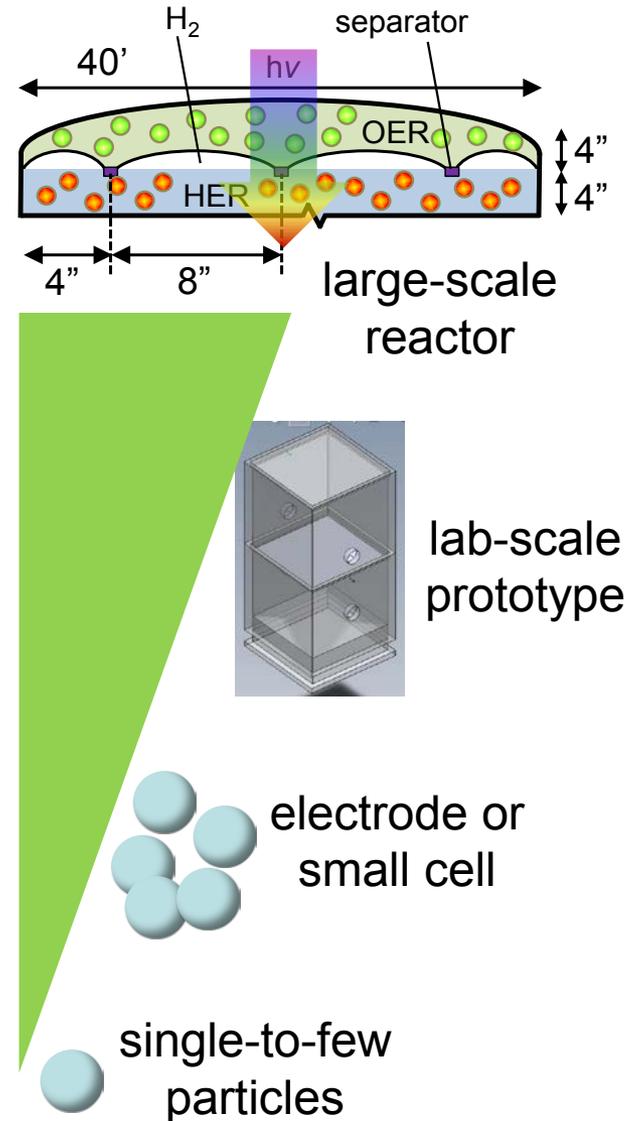
Approach: R&D



Photoelectrochemistry
and lab-scale reactors

Iterative computational and
experimental approach

Device physics
modeling and simulations



Approach: Milestones

Description of Milestone

Due Date (Quarter)

Percentage Complete

Task 1.0 Numerical modeling and simulation of new reactor design

| | | |
|---|------------------------------|------------|
| M1.1.1 Generate model that includes coupled charge transport, fluid flow, and Butler–Volmer kinetics. (AH) | November 1, 2015 (Q1) | 90% |
| M1.1.2 To the model, add advanced semiconductor charge transport, i.e. generation and recombination in the bulk and at surfaces. (AH) | August 1, 2016 (Q4) | 75% |
| D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH} . (AH) | August 1, 2016 (Q4) | 50% |
| M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow. (AH) | May 1, 2017 (Q7) | 5% |

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

| | | |
|---|----------------------------------|------------|
| M2.1.1 Particle evaluation apparatus and electrocatalyst deposition apparatus using bipolar electrochemistry. (AG, AJ) | February 1, 2016 (Q2) | 75% |
| M2.2.1 Maintain > 0.1% of initial redox shuttle concentration everywhere under conditions of day–night cycling. (AI) | May 1, 2016 (Q3) | 60% |
| M2.3.1 Identify material(s) that operate at a rate consistent with > 1% η_{STH} , in any form factor and using any redox couple. (AG) | November 1, 2016 (Q5) | 25% |
| M2.3.2 Demonstrate > 1% η_{STH} in electrode form factor. (AG) | February 1, 2017 (Q6) | 0% |
| M2.4.1 Demonstrate > 3 standard liters of H_2 from 8 hours of solar illumination. (AH) | August 1, 2017 (Q8 / end) | 0% |

Approach: Milestones

Description of Milestone

Due Date (Quarter)

Percentage Complete

Task 1.0 Numerical modeling and simulation of new reactor design

| | | |
|--|-----------------------|-----|
| M1.1.1 Generate model that includes coupled charge transport, fluid flow, and Butler–Volmer kinetics. (AH) | November 1, 2015 (Q1) | 90% |
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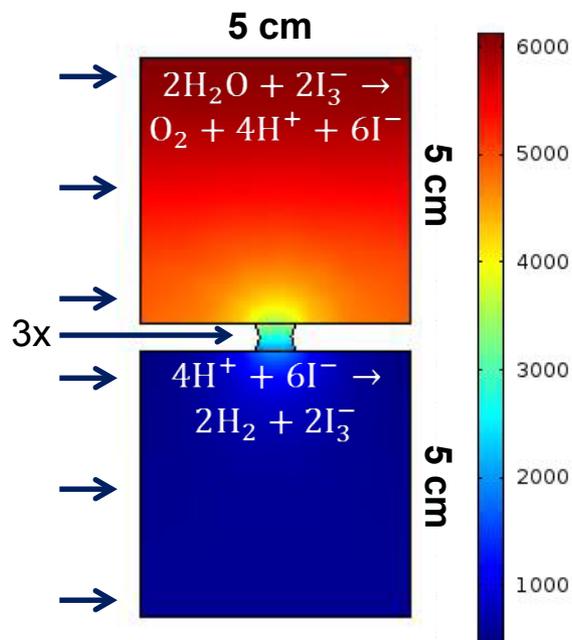
Significant Points and Discoveries

- Particles are not explicitly defined in the model.
- Migration around particles is appropriately neglected.
- Continuous Beer's Law absorption defines the maximum reaction rate along the reactor height as an input to the photodiode (or any) equation to drive the electrocatalytic reactions and determine rates of product formation (required iterative MATLAB and COMSOL communication).
- Large optical densities or thick compartments means particles close to the bottom are nearly dark and perform net shunting reverse reactions.

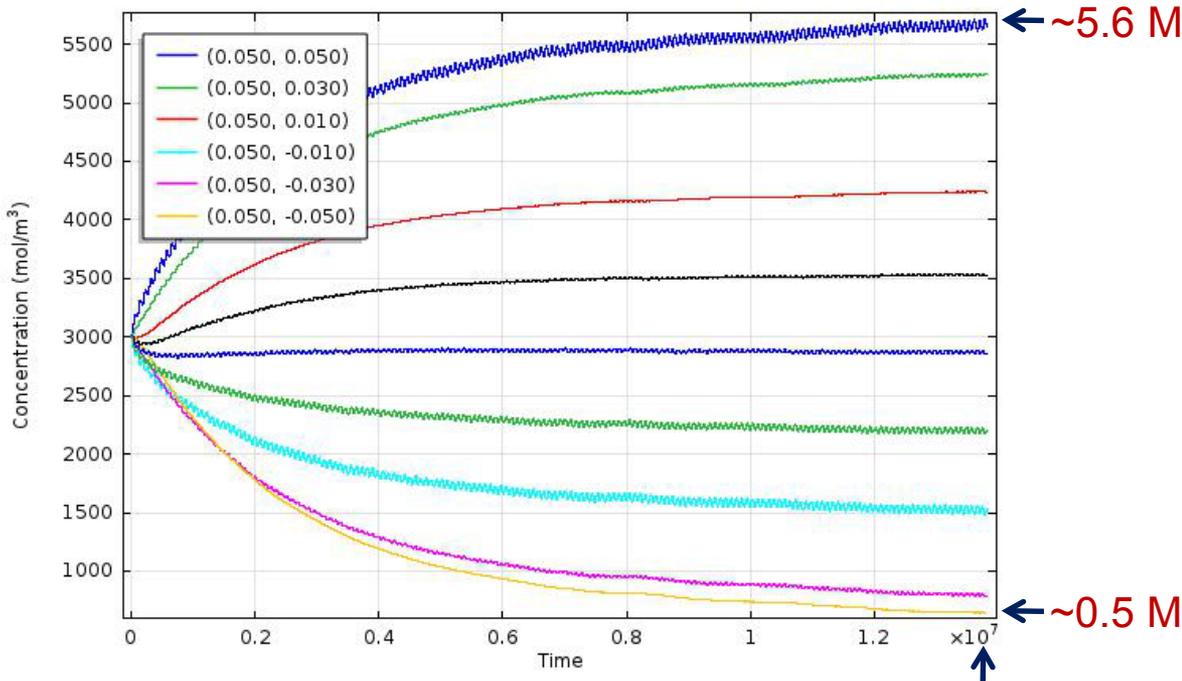


Accomplishments on Task 1.0

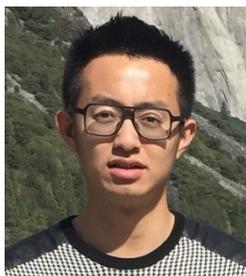
Iodide concentration @ $t = 160$ days



Time evolution of iodide concentration



Electrolyte is stable on at least half-a-year timescale



Yuanxun Shao
Chemical Engineer
(UCI Master's Student)

Toward M1.1.1

Reaction rate dictated by Beer's law absorption of solar irradiance scaled to $\eta_{\text{STH}} = 1\%$ and using complementary bandgap materials

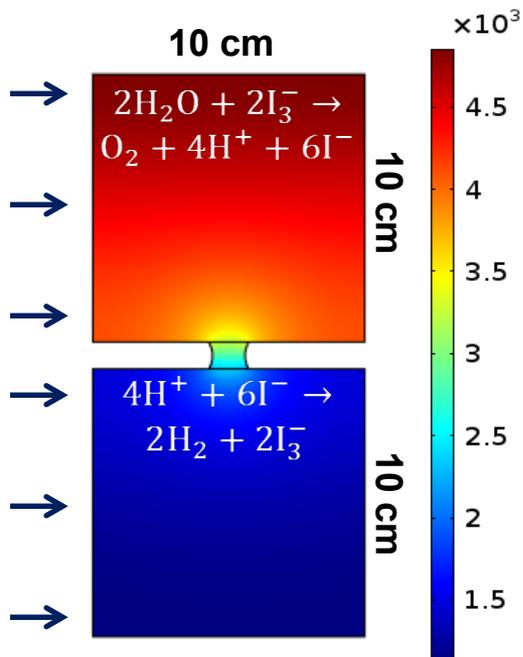
Additions to future models

- Photovoltage
- Electrocatalysis
- Sunlight absorption by redox shuttle
- Forced convection
- Separator porosity
- Non-proton counterion for redox shuttle

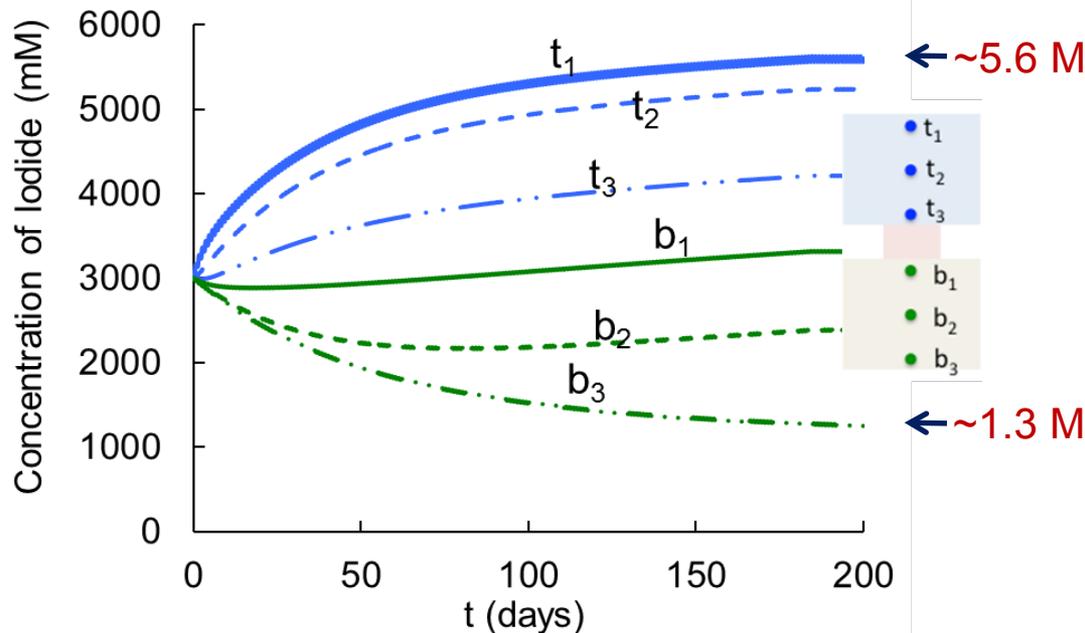


Accomplishments on Task 1.0

Iodide concentration @ $t = 200$ days



Time evolution of iodide concentration



Electrolyte is stable on at least half-a-year timescale

Toward M1.1.1 & M1.1.2

Reaction rate dictated by **experimental** Beer's law absorption of solar fluence (TiO_2 and $\text{Rh}:\text{SrTiO}_3$) to drive **ideal photodiode behavior** with coupled **Butler-Volmer electrocatalytic parameters**

Additions to future models

- Photovoltage ✓
- Electrocatalysis ✓
- Sunlight absorption by redox shuttle
- Forced convection
- Separator porosity
- Non-proton counterion for redox shuttle

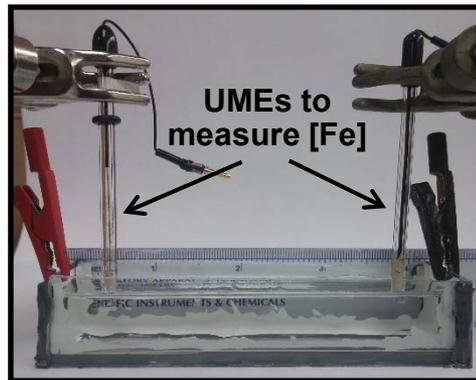
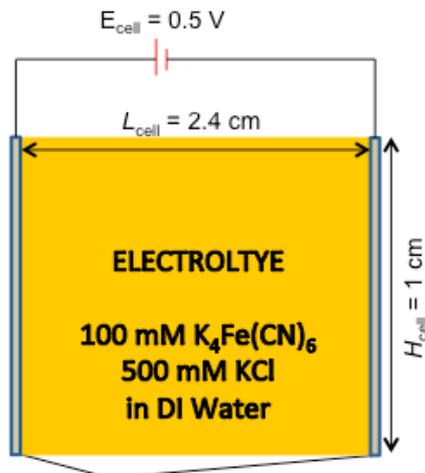


Rohini Bala Chandran
Mechanical Engineer
(LBNL Postdoc)



Accomplishments on Task 1.0

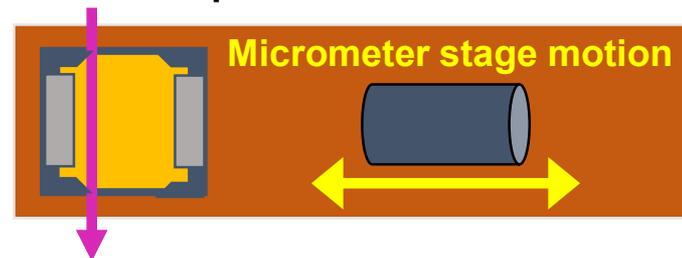
Side View



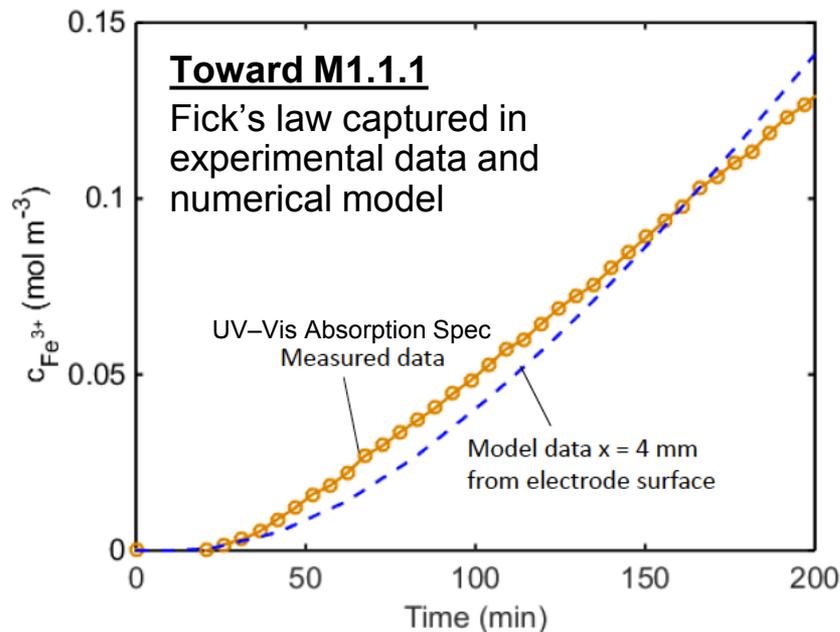
(new cell)

Top View

UV-Vis beam path



Theoretical diffusion observed experimentally



Rohini Bala Chandran
Mechanical Engineer
(LBNL Postdoc)



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



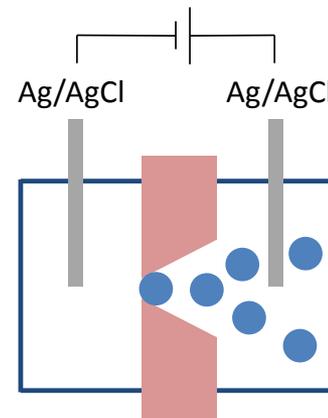
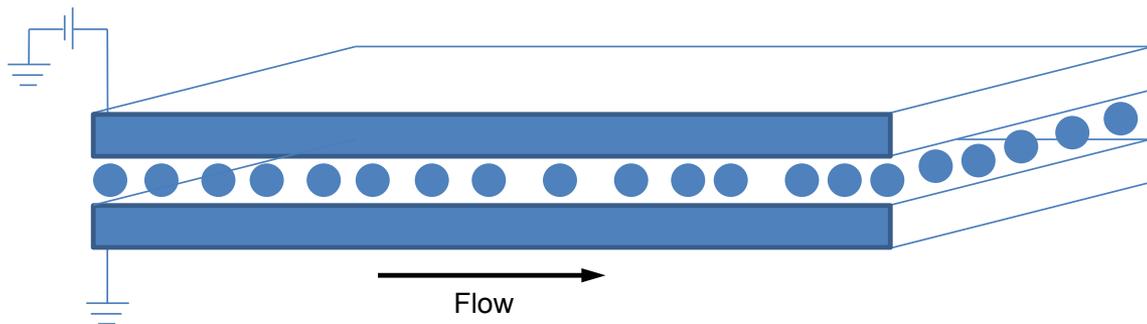
William Gaieck
Materials Scientist
(UCI Ph.D. Student)

Approach: Milestones

Description of Milestone

Due Date (Quarter)

Percentage Complete

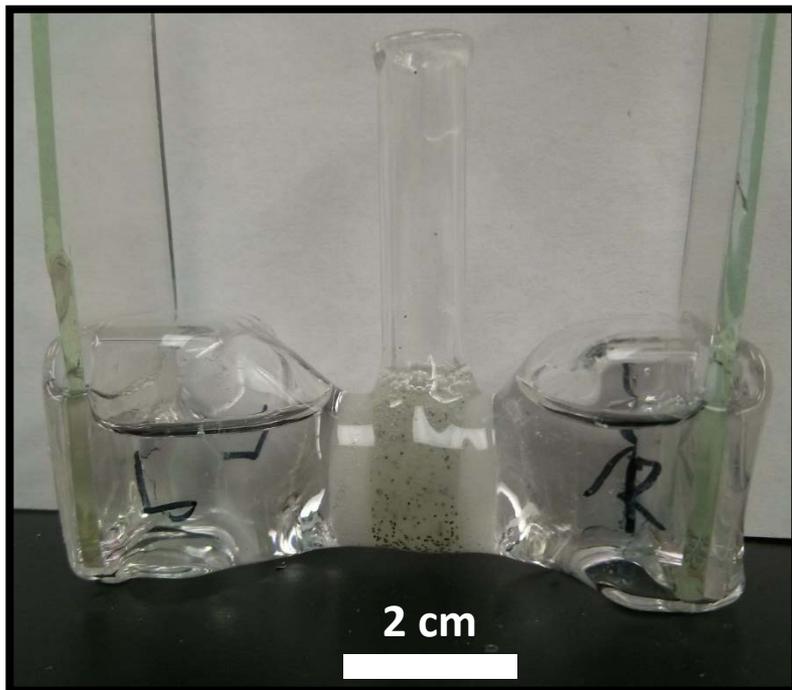


Task 2.0 Experimental evaluation of chemicals, materials, and reactors

| | | |
|---|---------------------------|-----|
| M2.1.1 Particle evaluation apparatus and electrocatalyst deposition apparatus using bipolar electrochemistry. (AG, AJ) | February 1, 2016 (Q2) | 75% |
| M2.2.1 Maintain > 0.1% of initial redox shuttle concentration everywhere under conditions of day–night cycling. (AI) | May 1, 2016 (Q3) | 60% |
| M2.3.1 Identify material(s) that operate at a rate consistent with > 1% η_{STH} , in any form factor and using any redox couple. (AG) | November 1, 2016 (Q5) | 25% |
| M2.3.2 Demonstrate > 1% η_{STH} in electrode form factor. (AG) | February 1, 2017 (Q6) | 0% |
| M2.4.1 Demonstrate > 3 standard liters of H_2 from 8 hours of solar illumination. (AH) | August 1, 2017 (Q8 / end) | 0% |



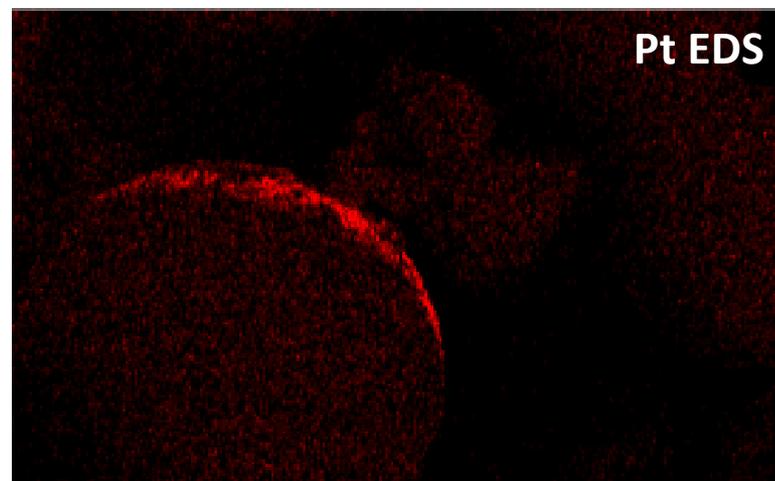
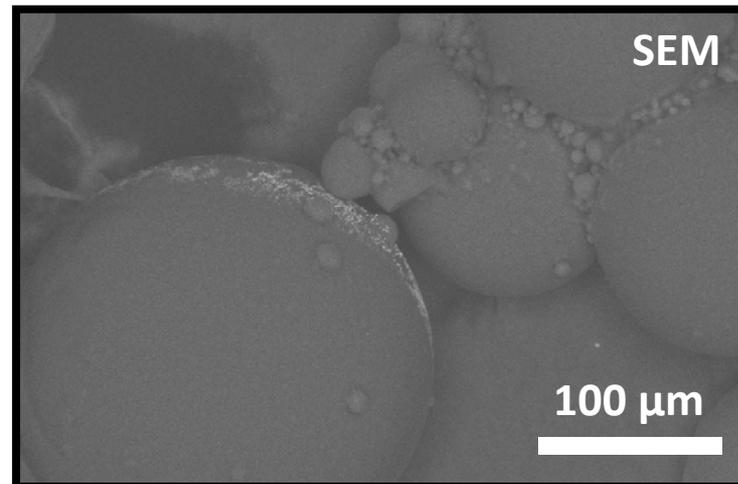
Accomplishments on Task 2.0



2-electrode measurement



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

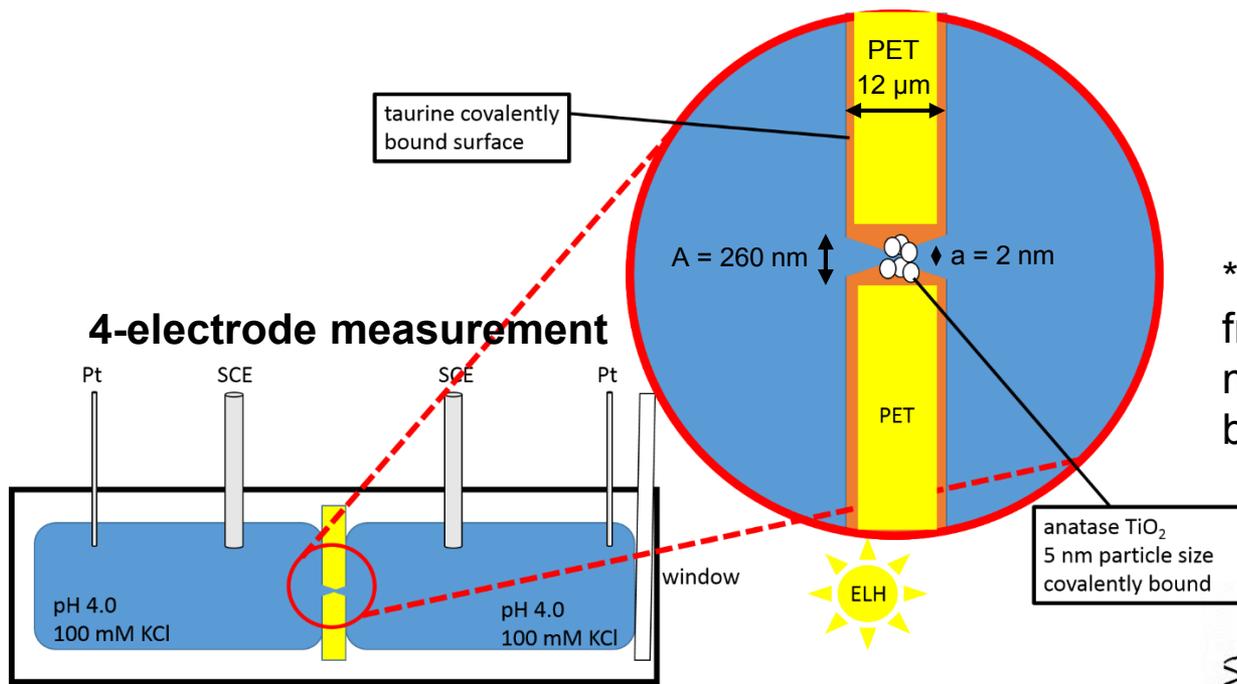


Vitreous carbon particles with
bipolar Pt electrodeposition
($E_{app} = 200$ V for 1.5 min)

Deposition of electrocatalysts on < 400 μm diameter carbon



Accomplishments on Task 2.0



* Similar behavior observed from V_{oc} data on the microsecond timescale and binned into histograms

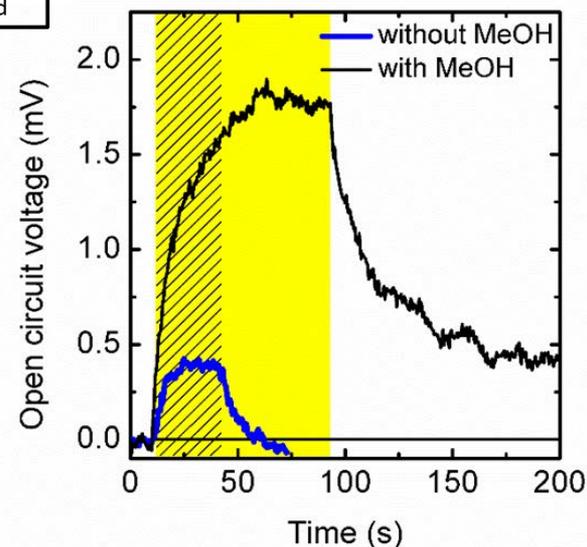


Christopher Sanborn
Organic Chemist
(UCI Ph.D. Student)



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

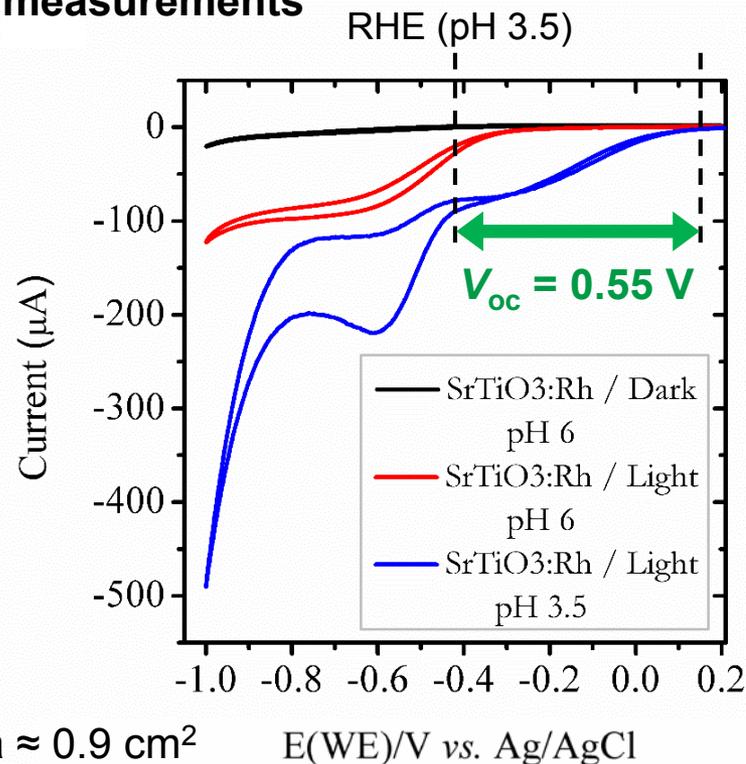
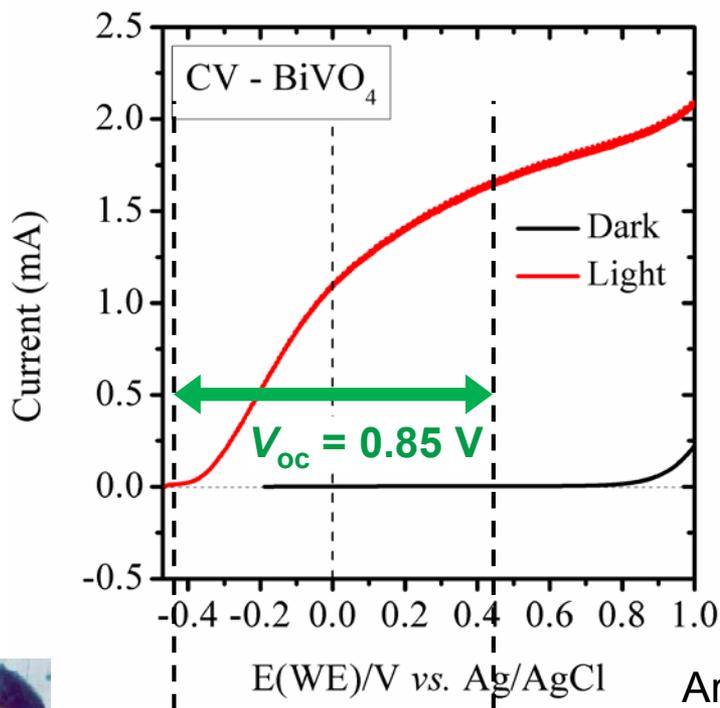
Observed photovoltage from “single” particle(s) indicates charging due to conduction-band electrons





Accomplishments on Task 2.0

3-electrode measurements



Houman Yaghoubi
Electrical Engineer
(UCI Postdoc)

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

Response to previous year reviewers' comments

This project was not reviewed last year.

Collaborations

Primary team members (funded)

- Lawrence Berkeley National Laboratory (Federal Lab) & Joint Center for Artificial Photosynthesis (DOE Hub)
 - » **Adam Weber (sub-recipient)**: Core numerical device-physics modeling and simulation effort, specifically chemical engineering and multi-physics
- California Institute of Technology (University) & Joint Center for Artificial Photosynthesis (DOE Hub)
 - » **Chengxiang Xiang (sub-contracted advisor)**: Expertise in numerical device-physics modeling and simulation effort, specifically semiconductor physics and ray tracing

Additional team members with expertise in particle materials synthesis (unfunded)

- Kyoto University, **Ryu Abe (Rh:SrTiO₃, BiVO₄)**
- Tokyo University of Science, **Akihiko Kudo (Rh:SrTiO₃, BiVO₄)**
- University of California, Davis, **Frank Osterloh (Rh:SrTiO₃, BiVO₄)**
- University of California, Riverside, **Phil Christopher (GaN:ZnO)**
- University of Houston, **Jiming Bao (CoO)**
- University of Tokyo, **Kazunari Domen (GaN:ZnO)**



Remaining Challenges and Barriers

Task 1.0 Numerical modeling and simulation of new reactor design

- Introduce fluid flow into the model to enable simulation of forced convection, e.g. by electrolyte pumping.
 - Introduce advanced semiconductor charge transport into the model, i.e. generation and recombination in the bulk and at surfaces, to more accurately model the particle photophysics.
 - **Go/No-Go Decision Point: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH} over time.**
 - Introduce electromagnetic wave propagation, thermal effects, and multi-phase flow into the model to make it more realistic.
-

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

- Use bipolar electrochemistry to measure single particle photovoltages, as inputs into the numerical models.
- Use bipolar electrochemistry to deposit electrocatalysts on sub-micron-sized particles.
- Maintain > 0.1% of initial redox shuttle concentration everywhere in the reactor under conditions of day–night cycling as an indicator of long-term availability of the redox shuttle.
- Identify material(s) that operate at a rate consistent with > 1% η_{STH} , in any form factor and using any redox couple, and then in electrode form factor, as prerequisites to the final deliverable.

Final Deliverable: Demonstrate > 3 standard liters of H₂ from 8 hours of solar illumination.

Proposed Future Work

2015–2016 Objective (FY16): Numerically demonstrate the feasibility of a reactor that exhibits $\eta_{\text{STH}} = 1\%$

| Description of Milestone – Solution | Due Date (Quarter) | Percentage Complete |
|-------------------------------------|--------------------|---------------------|
|-------------------------------------|--------------------|---------------------|

Task 1.0 Numerical modeling and simulation of new reactor design

D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH} – **Introduce forced convection**

August 1, 2016 (Q4)

50%

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

M2.3.1 Identify material(s) that operate at a rate consistent with $> 1\%$ η_{STH} , in any form factor and using any redox couple – **Explore alternative syntheses for high-quality materials**

November 1, 2016 (Q5)

25%

Proposed Future Work

2015–2016 Objective (FY16): Numerically demonstrate the feasibility of a reactor that exhibits $\eta_{\text{STH}} = 1\%$

Project Objective (FY17): Experimentally validate a laboratory-scale particle suspension reactor as a scalable technology for solar H_2 production

| Description of Milestone – Solution | Due Date (Quarter) | Percentage Complete |
|-------------------------------------|--------------------|---------------------|
|-------------------------------------|--------------------|---------------------|

Task 1.0 Numerical modeling and simulation of new reactor design

| | | |
|---|---------------------|-----|
| D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH} – Introduce forced convection | August 1, 2016 (Q4) | 50% |
|---|---------------------|-----|

| | | |
|---|------------------|----|
| M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow – Introduce multiple physics | May 1, 2017 (Q7) | 5% |
|---|------------------|----|

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

| | | |
|---|-----------------------|-----|
| M2.3.1 Identify material(s) that operate at a rate consistent with $> 1\%$ η_{STH} , in any form factor and using any redox couple – Explore alternative syntheses for high-quality materials | November 1, 2016 (Q5) | 25% |
|---|-----------------------|-----|

| | | |
|---|-----------------------|----|
| M2.3.2 Demonstrate $> 1\%$ η_{STH} in electrode form factor – Introduce electrocatalysts by photoelectrochemical deposition | February 1, 2017 (Q6) | 0% |
|---|-----------------------|----|

| | | |
|---|---------------------------|----|
| M2.4.1 Demonstrate > 3 standard liters of H_2 from 8 hours of solar illumination – Combine particles and reactor designs | August 1, 2017 (Q8 / end) | 0% |
|---|---------------------------|----|

Project Summary

Project Objective: **Experimentally validate** a laboratory-scale particle suspension reactor as a scalable technology for solar H₂ production

| | |
|----------------------------------|--|
| Relevance | Techno-economic analyses of side-by-side particle suspension compartments suggest that H ₂ cost may be inexpensive. |
| Approach | Stack the compartments to realize the tandem efficiency advantage and shorten the mass transport distance so that fewer pumps and pipes are needed. |
| Technical Accomplishments | Using a validated device physics model, demonstrated stable operation of a 1% STH stacked tandem reactor for over 200 days. Also used bipolar electrochemistry to deposit electrocatalysts and measure the photoresponse of single-to-few particles jammed in a plastic sheet. Also, synthesized and characterized efficient photoelectrodes consisting of Rh-modified SrTiO ₃ or BiVO ₄ . |
| Collaborations | Several, including modeling experts and particle synthesis experts. |
| Proposed Future Work | Add additional device physics to the numerical models and synthesize high quality metal-oxide particles. |

Technical Backup Slides

Motivation

Table 5 Summary of all direct capital expenditures and installation costs for the four different 1 TPD net H₂ 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 |

Materials options: “Type 2”

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 | | | Quantum yield, % (wavelength (nm)) | Year ^{ref} |
|--|----------------------------------|--|-------------------------------------|--|--|---------------------------------------|---------------------------------------|------------------------------------|---------------------------|
| | | | | | Illumination ^b (irradiance (mW cm ⁻²), wavelength (nm)) | H ₂ , μmol h ⁻¹ | O ₂ , μmol h ⁻¹ | | |
| 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 ₂ N | Pt (0.3) | WO ₃ | Pt (0.5) | NaI (5) | Xe (n.r., >420) | ~5.5 | ~2.5 | n.r. | 2008 ¹⁵² |
| BaTaO ₂ N | 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 |
| Domen ZrO₂-TaON | Pt (1.0, 0.5)^d | WO₃ | Pt (0.5) | NaI (1.0, 0.5)^d | Xe (n.r., 420–800) | 33 | 16 | 6.3 (420.5) | 2010¹⁵³ |
| ZrO ₂ -TaON | Pt (1) | TiO ₂ -Ta ₃ N 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 ₄ Nb ₆ O 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 ₄ Nb ₆ O 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 |

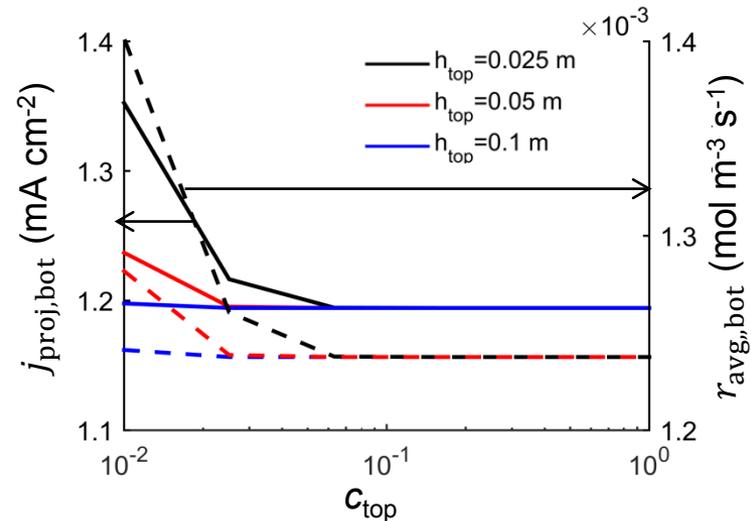
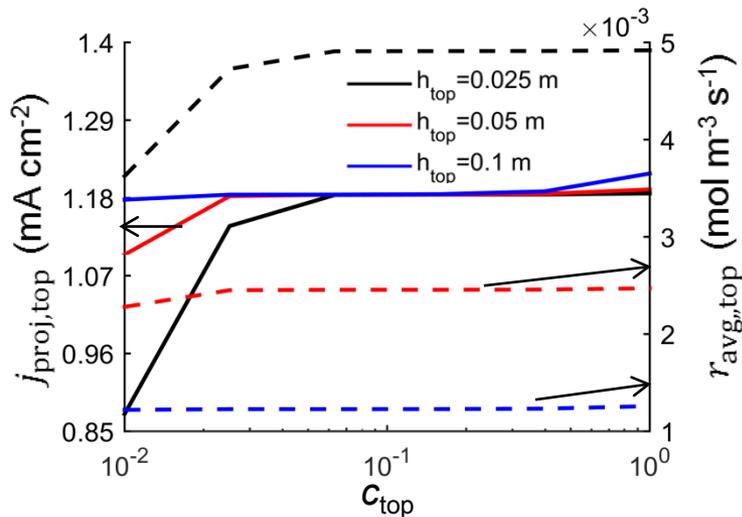
Table 5 Reports of visible-light-driven water splitting using suspensions with two particles and a non-iodine-based redox shuttle^a

| HER light absorber | HER cocatalyst (wt%) | OER light absorber | OER cocatalyst | Aqueous electrolyte (concentration (mM), pH) | Activity measurement | | | Quantum yield, % (wavelength (nm)) and/or STH efficiency, % | Year ^{ref} |
|--|----------------------|----------------------------------|----------------|---|--|---------------------------------------|---------------------------------------|---|---------------------------|
| | | | | | Illumination ^b (irradiance (mW cm ⁻²), wavelength (nm)) | H ₂ , μmol h ⁻¹ | O ₂ , μmol h ⁻¹ | | |
| SrTiO ₃ :Rh | Pt (0.5) | Bi ₂ MoO ₆ | None | FeCl ₃ (2, 2.4 w/ H ₂ SO 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 ₂ SO ₄) | Xe (n.r., >420) | ~24 | ~11 | 0.5 (420) | 2004 ⁶⁸ |
| Kudo & Abe (+UCD) SrTiO₃:Rh | Ru (1) | BiVO₄ | None | FeCl₃ (2, 2.4 w/ H₂SO₄) | Xe (100, >420) | 130 | 64 | 4.2 (420), 0.1 STH | 2013¹⁶⁶ |
| 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 |

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Effects of Top Compartment Photocatalyst Concentration and Reactor Height

| Model Parameter | Top Values | (Bot)tom Values |
|---|---|---|
| Compartment height, h | 0.025, 0.05, 0.1 m | 0.1 m |
| Photocatalyst concentration, c | 0.01 – 1 g L ⁻¹ | 0.002 g L ⁻¹ |
| Photocatalyst bandgap, E_g | 3.1, 2.5 eV | 2.5 eV |
| OER/HER reverse saturation current density, j_r | 10 ⁻¹⁰ – 10 ⁻¹⁸ A m ⁻² | 10 ⁻¹⁰ – 10 ⁻¹⁸ A m ⁻² |
| OER/HER exchange current density, j_o | 10 ⁻⁴ A m ⁻² | 1.5 A m ⁻² |

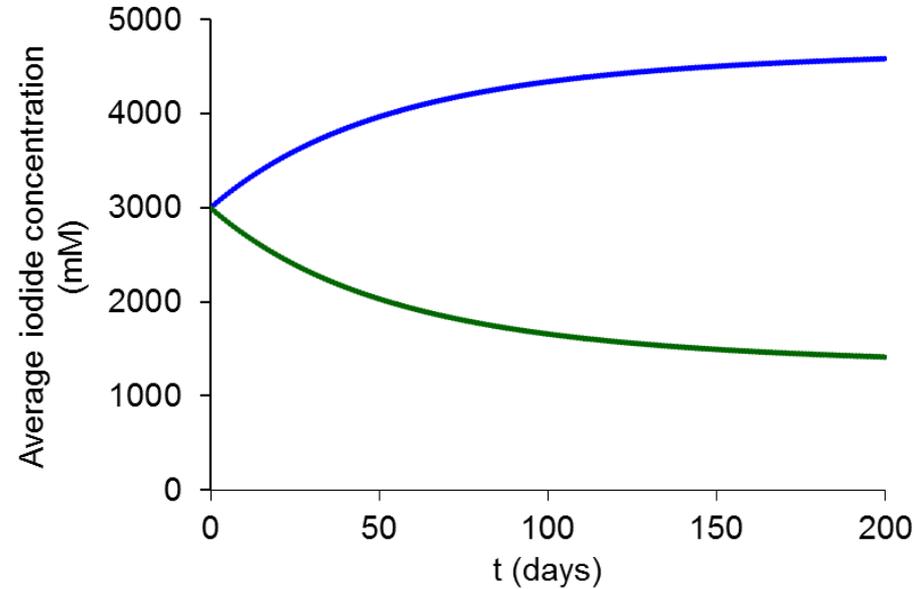
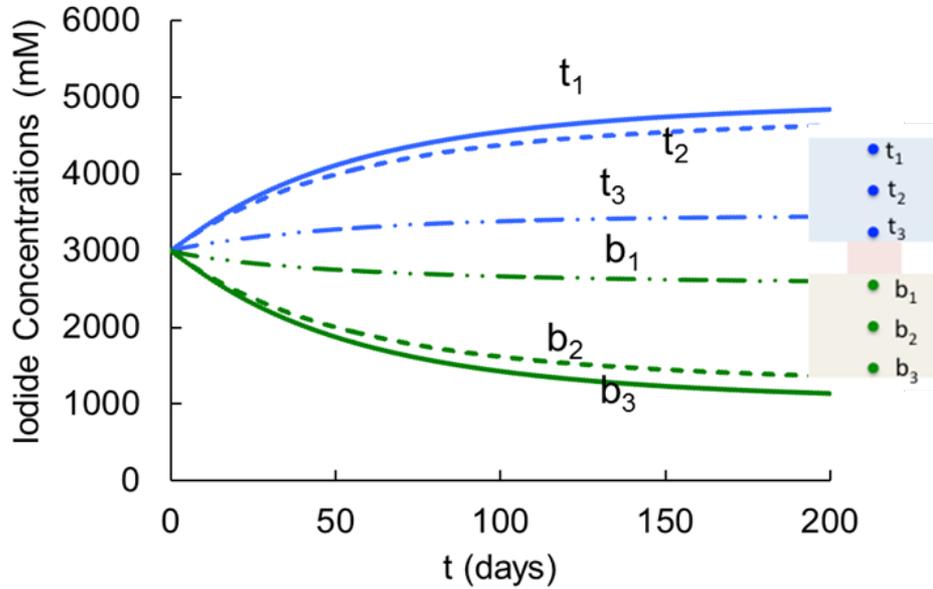


* Mass transport effects not included in these simulations

Model Parameters for Transient Simulations

| | TOP (OER) | BOTTOM (HER) |
|-----------------------------|-------------------------------------|-------------------------------------|
| Photocatalyst Concentration | TiO ₂ 0.01 g/L | SrTiO ₃ :Rh 0.002 g/L |
| Height | 10 cm | 10 cm |
| j_r | 10 ⁻¹⁸ A m ⁻² | 10 ⁻¹⁰ A m ⁻² |
| j_o | 10 ⁻⁴ A m ⁻² | 1.5 A m ⁻² |
| A_0 | 14.2 m ² m ⁻³ | 8.6 m ² m ⁻³ |
| Particle Diameter | 1 μm | 1 μm |

Model with Complete Scattering



* Assumed homogeneous reaction rates