PD125

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.

Thursday, June 8, 2017

US DOE, EERE, FCTO, Annual Merit Review

Overview

Project Timeline

- Start date: August 1, 2015
- New end date: January 31, 2018 (30-month period of performance)

Project Budget

•	Total budget:	\$1,248,063
	 Federal funds: 	\$ 993,759

- Federal funds:
- UCI cost share: S
- Funding by year (UCI only)
 - Year 1 spent: 410,258 S

254,304

- Year 1 budget: \$ 412,943
- \$ 93,400 – Year 2 spent*:
- Year 2 budget: \$ 300,901

* as of 3/31/2017

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 $\geq 10x$
- Could meet MYRD&D targets
 - High-efficiency materials
 - Large reductions in materials costs



Particle-slurry Design

- 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

Lower III-V costs Optical concentration Anti-reflection

> **III-V PEC** systems

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

> Thin-film PEC systems

Higher TRL

Absorbers and interfaces processing compatibility

HydroGen Consortium

Sunlight to H Interfaces ntalv

TH efficiency

tis unomics bisessment https://www.executiong.challengestropy.com/ bit/time/consecutiong.challengestropy.com/ bit/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.challengestropy.com/ bis/time/consecutiong.com/ bis/time/c

Cooking Outward: Unique materials de

Particle PEC systems

Lower TRL

Reactor designs Selective catalysis Gas separation Mass transfer

Relevance: Concept

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

<u>August 2016 Objective</u>: **Numerically demonstrate** that the *new reactor design* can sustain $a \ge 1\%$ solar-to-hydrogen (STH) conversion efficiency

	MY	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 physics and techno-economics of new tandem two-compartment particle suspension reactor designs Fabricate model reactors with <i>in situ</i> 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 of selective electrocatalysis



New Stacked-Reactor Design



Directed Technologies, Inc., DOE Report, 2009 & DOE H2A Analysis, https://www.hydrogen.energy.gov/h2a_production.html 6



Approach: R&D Materials Choice

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

					Aguagus	Activity measurement				
HER light absorber	HER cocatalys (wt%)	OER st light absorb	OER cocat er (wt%	talyst)	electrolyte (concentration (mM), pH)	Illumination ^{b} (irradiance (mW cm ^{-2}), wavelength (nm))	H ₂ , μmol h ⁻¹	Ο ₂ , µmol h ⁻¹	Quantum yield, % (wavelength (nm))	Year ^{ref}
TaON CaTaO ₂ N $BaTaO_2N$ TaON ZrO ₂ -TaON ZrO ₂ -TaON SrTiO ₃ :Cr,Ta Coumarin- H ₄ Nb ₆ O ₁₇ Carbazole- H ₄ Nb ₆ O ₁₇ BaTiO ₃ :Rh	Pt (0.3) Pt (0.3) Pt (0.3) Pt (0.3) Pt (0.3) Pt (1.0, 0 Pt (1) Pt (0.3) Pt (0.5) Pt (0.5) Pt (0.25)	$WO_3 WO_3 WO_3 TaON 0.5)^d WO_3 TiO_2-T WO_3 WO_3 WO_3 WO_3 WO_3$	$\begin{array}{c} & {\rm Pt} \ (0, \\ {\rm Pt} \ (0, \\ {\rm Pt} \ (0, \\ {\rm RuO}_2 \\ {\rm Pt} \ (0, \\ {\rm Ino}_2 \\ {\rm PtO}_x \\ {\rm IrO}_2 \\ {\rm Pt} \ (0, \\ {\rm IrO}_2 \\ {\rm Pt} \ (0, \\ {\rm IrO}_2 \\ {\rm Pt} \ (0, \\ {\rm PtO}_x \\ {\rm PtO}_x \end{array}$.5) .5) .5) .2 (0.3) .5) (0.5) and .5) (0.5) and .5) (0.5 (Pt))	NaI $(5, 7)$ NaI (5) NaI (5) NaI $(1, 6)$ NaI $(1.0, 0.5)^d$ NaI (0.1) NaI $(10, 4)$ KI (5) NaI (10)	Xe (n.r., >420) ^c Xe (n.r., >420) Xe (n.r., >420) Xe (n.r., >420) Xe (n.r., >420) Xe (n.r., >420-800) Xe (n.r., >420) Xe (n.r., >420) Xe (n.r., >410) Xe (n.r., >420) Xe (n.r., >420)	$24 \\ \sim 5.5 \\ \sim 6.5 \\ \sim 10 \\ 33 \\ \sim 7 \\ 32 \\ 2.2 \\ 1.7 \\ 1.7 $	$ \begin{array}{c} 12 \\ \sim 2.5 \\ \sim 3.0 \\ \sim 4 \\ 16 \\ \sim 1 \\ 16 \\ 0.9 \\ 0.7 \\ 0.6 \\ \end{array} $	0.4 (420) n.r. $\sim 0.1 (420-440)$ 0.1-0.2 (420) 6.3 (420.5) n.r. 1.5 (420) 0.05 (480) n.r. 0.5 (420)	$\begin{array}{c} 2005^{151}\\ 2008^{152}\\ 2008^{152}\\ 2008^{155}\\ \textbf{2010}^{153}\\ 2010^{156}\\ 2013^{149}\\ 2013^{164}\\ 2013^{164}\\ 2014^{154} \end{array}$
Table 5 Re	eports of vi	isible-light-d	riven water	splitting u	ising suspension	s with two particles and a	non-iodine	e-based rec	ox shuttle ^a	
						Activity measurement				
HER light absorber	HER cocatalyst (wt%)	OER light absorber	OER cocatalyst	Aqueous electroly (concent (mM), p	s rte tration H)	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 ^{ref}
SrTiO ₃ :Rh SrTiO ₃ :Rh SrTiO ₃ :Rh	Pt (0.5) Pt (0.5) Ru (1) Bu (0.7)	Bi ₂ MoO ₆ WO ₃ BiVO ₄	None None None	FeCl ₃ (2 FeCl ₂ (2 FeCl ₃ (2	, 2.4 w/ H ₂ SO ₄) , 2.4 w/ H ₂ SO ₄) , 2.4 w/ H ₂ SO ₄)	Xe (n.r., >420) Xe (n.r., >420) Xe (100, >420) Xe (100, >420)	~ 20 ~ 24 130 7.9	~ 10 ~ 11 64 3.5	0.2 (440) 0.5 (420) 4.2 (420), 0.1 STH	2004 ⁶⁸ 2004 ⁶⁸ 2013 ¹⁶⁶ 2013 ¹⁴⁴
	HER light absorber TaON CaTaO ₂ N $BaTaO_2N$ TaON ZrO ₂ -TaON SrTiO ₃ :Cr,Ta Coumarin- H ₄ Nb ₆ O ₁₇ Carbazole- H ₄ Nb ₆ O ₁₇ BaTiO ₃ :Rh Table 5 Re HER light absorber SrTiO ₃ :Rh SrTiO ₃ :Rh	HER light absorberHER cocatalys (wt%)TaON TaON CaTaO2N BaTaO2N TaON Pt (0.3) BaTaO2N Pt (0.3)TaON DaTaON Pt (0.3)TaON DaTaON Pt (0.3)TaON Pt (0.3)TaON Pt (0.3)TaON Pt (0.3)TaON Carbazole- Pt (0.5)H4Nb6O17 Carbazole- Pt (0.5)H4Nb6O17 BaTiO3:RhTable 5Reports of viTable 5Reports of viSrTiO3:Rh borberPt (0.5)SrTiO3:Rh SrTiO3:RhPt (0.5)SrTiO3:Rh SrTiO3:RhPt (0.5)SrTiO3:Rh Pt (0.5)Pt (0.5)SrTiO3:Rh Pt (0.5)	HER light absorberHER cocatalyst (wt%)OER light absorbTaON TaON CaTaO2N BaTaO2N TaONPt (0.3) Pt (0.3) Pt (0.3) TaON Pt (0.3) TaON Pt (0.3) TaON Pt $(1.0, 0.5)^d$ WO3 TaON TaON Pt $(1.0, 0.5)^d$ ZrO2-TaON SrTiO3:Cr,Ta Pt $(1.0, 0.5)$ Pt $(1.0, 0.5)^d$ WO3 To2-T SrTiO3:Cr,Ta Pt (0.3) WO3 Coumarin- Pt (0.5) WO3 H4Nb6O17 BaTiO3:RhPt (0.5) WO3 WO3 WO3 Table 5Table 5Reports of visible-light-dHER light absorberCocatalyst (wt%)HER light absorberOER cocatalyst light absorberSrTiO3:Rh SrTiO3:RhPt (0.5) Pt (0.5) SrTiO3:Rh SrTiO3:RhPt (0.5) Pt (0.5) SrTiO3:Rh SrTiO3:RhPt (0.5) Pt (0.5) SrTiO3:Rh SrTiO3:RhPt (0.5) Pt (0.5) SrTiO3:Rh SrTiO3:RhPt (0.5) Pt (0.5) Bi2MOO6 Bi2MO2	HER light absorberHER (wt%)OER light absorberOER (wt%)TaON CaTaO2N BaTaO2N Pt (0.3)Pt (0.3) Pt (0.3)WO3 WO3 Pt (0Pt (0BaTaO2N Pt (0.3)Pt (0.3) WO3 Pt (0.3)WO3 Pt (0Pt (0TaON Pt (0.3)Pt (0.3) TaON Pt (0.3)TaON Pt (0.3)RuO2 Pt (0ZrO2-TaON Pt (1)Pt (1.0, 0.5)d TiO2-Ta3N5Pt (0ZrO2-TaON Pt (1)Pt (1.0, 0.5)d TiO2-Ta3N5Pt (0ZrO2-TaON Pt (1)Pt (0.3) TiO2-Ta3N5Pt (0ZrO2-TaON Pt (1)Pt (0.3) TiO2-Ta3N5Pt (0ZrO2-TaON Coumarin- Pt (0.5)WO3 WO3 PtO2PtO2 Pt (0Carbazole- Pt (0.5)Pt (0.5) WO3 WO3IrO2 Pt (0BaTiO3:Rh absorberPt (0.25) wO3 Bi2MOQ6 WO3 NonePt (0.5) NoneHER light absorberOER (wt%)OER absorberOER cocatalystFTIO3:Rh FT (0.5)Pt (0.5) WO3 NoneNone WO3 NoneNone	HER light absorberHER cocatalyst (wt%)OER light absorberOER cocatalyst absorberTaON CaTaO_2N BaTaO_2NPt (0.3) Pt (0.3) Pt (0.3) Pt (0.3) Pt (0.5) TaON TaON Pt (0.3) Pt (0.3) Pt (0.5) TaON Pt (0.5) TaON Pt (0.3) Pt (0.5) TaON Pt (0.5) TaON Pt (0.3) Pt (0.5) TaON Pt (0.5) TaON Pt (0.5) Pt (0.5) TaON Pt (0.5) Pt (0.5) TaON Pt (1) SrTiO_3:Cr,Ta Pt (0.5) Pt (0.5) Coumarin- Pt (0.5) Pt (0.5) Carbazole- Pt (0.5) Pt (0.5) Pt (0.5) BaTiO_3:Rh Pt (0.25) WO_3 PtO_x $(0.5 (Pt))$ Aqueous Pt (0.5) PtO_x $(0.5 (Pt))$ Table 5 Reports of visible-light-driven water splitting to absorber (wt%) absorber cocatalyst light absorber Cocatalyst light Pt (0.5) SrTiO_3:Rh Pt (0.5) Bi2MOO_6 None FeCl_3 (2 SrTiO_3:Rh Pt (0.5) Ru (1) BiVO_4None FeCl_2 (2 SrTiO_3:Rh Pt (0.5) Ru (1) BiVO_4	HER light absorberHER cocatalyst (wt%)OER light absorberOER cocatalyst (wt%)Aqueous electrolyte (concentration (mM), pH)TaON TaON Pt (0.3)Pt (0.3) WO3 WO3 Pt (0.5)NaI (5, 7) NaI (5)NaI (5, 7) NaI (5)BaTaO2N BaTaO2N Pt (0.3)Pt (0.3) WO3 TaON Pt (0.3)Pt (0.5) NaI (5)NaI (1.6) NaI (1.6)ZrO2-TaON ZrO2-TAON Pt (1.0, 0.5)dPt (0.5) WO3 Pt (0.5)NaI (1.0, 0.5)d NaI (1.0, 0.5)dZrO2-TaON Pt (1.1)Pt (1.0, 0.5)d TiO2-Ta3N5 Pt (0.5)NaI (1.0, 0.5)d NaI (1.0, 0.5)dZrO2-TaON Pt (1.1)Pt (0.5) TiO2-Ta3N5 Pt (0.5)NaI (1.0, 0.5)d NaI (1.0, 0.5)dZrO2-TaON Pt (1.1)Pt (0.5) TiO2-Ta3N5 Pt (0.5)NaI (1.0, 0.5)d NaI (1.0, 0.5)dSrTiO3:Cr,Ta Pt (0.5)Pt (0.5) WO3NaI (0.1) ToO2 (0.5)NaI (10, 4) NaI (10, 4)Coumarin- Pt (0.5)Pt (0.5) WO3IrO2 (0.5) and KI (5) Pt (0.5)BaTiO3:Rh Pt (0.25)WO3PtOx (0.5 (Pt)) NaI (10)Table 5Reports of visible-light-driven water splitting using suspensionHER light absorber (wt%)OER absorber cocatalyst (mM), pH)SrTiO3:Rh SrTiO3:Rh Pt (0.5)Bi2MOO6 WO3 NoneNone FeCl3 (2, 2.4 w/ H2SO4) FeCl3 (2, 2.4 w/ H2SO4)SrTiO3:Rh SrTiO3:Rh Ru (1)BiVO4 BiVO4None NoneFeCl3 (2, 2.4 w/ H2SO4)	HER light absorberHER cocatalyst (wt%)OER light absorberOER cocatalyst (wt%)OER cocatalyst (wt%)Aqueous electrolyte (concentration (mM), pH)Activity measurement Illumination ^b (irradiance (mW cm ⁻²), wavelength (nm))TaON CaTaO_2N BaTaO_2N Pt (0.3)WO_3 WO_3Pt (0.5) Pt (0.5)NaI (5, 7) NaI (5)Xe (n.r., >420) Xe (n.r., >420)TaON Data Pt (0.3)WO_3 WO_3Pt (0.5) Nol (5)NaI (1, 6) NaI (1, 0, 0.5)Xe (n.r., >420) Xe (n.r., >420)TaON TO_2-TaON TO_2-TaON Pt (1)TiO_2-Ta_3N_5 TiO_2-Ta_3N_5Ir (0, 5) Nol (0.5)NaI (1, 0, 0.5) NaI (0.1)Xe (n.r., >420) Xe (n.r., >420)ZrO_2-TaON Pt (1)Pt (1) TiO_2-Ta_3N_5Tir (5) Nol (0.5)NaI (1, 0, 0.5) NaI (10, 4)Xe (n.r., >420) Xe (n.r., >420)SrTiO_3:Cr,Ta Uarbazole Pt (0.5)WO_3 WO_3PtO_x (0.5) Pt (0.5)NaI (10, 4) Xe (n.r., >410) Pt (0.5)Xe (n.r., >410) Ye (0.5)Table 5 Reports of visible-light-driven (wt%)WO_3 absorberPtO_x (0.5 (Pt)) (concentrationNaI (10) Xe (n.r., >420)Table 5 SrTiO_3:Rh StriO_3:RhPt (0.5) BigMO_6 SrTiO_3:RhBight absorberOER Cocatalyst (concentrationAqueous electrolyte (concentrationFECI3 (2, 2.4 w/H2SO4) SrTiO_3:RhPt (0.5) BigMO_6None NoneFeCI3 (2, 2.4 w/H2SO4) FeCI3 (2, 2.4 w/H2SO4) Ye (10, >420)SrTiO_3:Rh SrTiO_3:RhRu (1) BiV(0.5)None WO_3FeCI_3 (2, 2.4 w/H2SO4) FeCI_3 (2, 2.4	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

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 simulation	ons of new reactor	⁻ design
M1.1.2 To the model, add advanced semiconductor charge transport, i.e. generation and recombination in the bulk and at surfaces. (AH) – effective reverse saturation reaction rate implemented	August 1, 2016 (Q4)	100%
D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH} . (AH, AI) – sustainable reactor demonstrated, with no required pumps or pipes	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 physical processes has been implemented in part	August 1, 2017 (Q8)	80%

Accomplishments: Go, with Q/QH₂



Accomplishments: Go, with IO₃⁻/I⁻



Separator thickness and porosity limit H₂/O₂ crossover

Accomplishments: Convection



Thermal mixing due to sunlight absorption by water; not in reactor model yet



Rohini Bala Chandran Mechanical Engineer (LBNL Postdoc)

Assumptions

- Neglected spatial density gradients due to inhomogeneous particle concentrations, i.e. $\frac{d\rho}{dc}\frac{dc}{dy}$
- Volumetric heat source, q_s , obtained through sunlight absorption by water (Beer's law at λ > 700 nm)
- Spatially uniform reaction rate, r_i , and boundary flux, N_0 , are consistent with a 1% STH efficiency
- o Steady-state conditions evaluated without diurnal illumination

Approach: Milestones

Description of Milestone	Due Date (Quarter)	Percentage Complete
Task 1.0 Numerical modeling and simulation	ons of new reactor	[.] design
M1.1.2 To the model, add advanced semiconductor charge transport, i.e. generation and recombination in the bulk and at surfaces. (AH) – effective reverse saturation reaction rate implemented	August 1, 2016 (Q4)	100%
D1.1.1 Go/No-Go Decision: Using 80% less pipes and 80% less pumping energy, verify 1% η_{STH} . (AH, AI) – sustainable reactor demonstrated, with no required pumps or pipes	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 physical processes has been implemented in part	August 1, 2017 (Q8)	80%

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. (AJ, AG) – BiVO₄ with aqueous electrolyte & Rh:SrTiO₃ with redox shuttle	February 1, 2017 (Q6)	100%	
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 ; alternative HER particles, syntheses, and dopants are being explored	May 1, 2017 (Q7)	25%	
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 reactor with 10x smaller illumination area than final deliverable; detected H ₂ from smaller reaction vessel using mass spectrometry	February 1, 2018 (Q10 / end)	15%	13

Accomplishments: Rh:SrTiO₃ HER



(XPS, UPS, SEM, EDS, XD, DRS, Raman, DLS)



- Rh:SrTiO₃ state-of-the-art HER nanoparticle material
- Holes oxidize H₂ prior to being collected in the circuit

Selective reactivity (e.g. no H_2 oxidation) is a big challenge for photocatalysts





Accomplishments: Rh:SrTiO₃ HER



Accomplishments: WO₃ OER

- WO_3 state-of-the-art OER particle material in acid
- J-E behavior is very similar with and without O_2
- Interesting photocurrent behavior with added Fe(II) redox shuttle (data reported here is light current density minus dark current density)







<u>William Gaieck</u> Materials Scientist (UCI Ph.D. Student)

Accomplishments: WO₃ OER

- WO_3 state-of-the-art OER particle material in acid
- J-E behavior is very similar with and without O_2
- Interesting photocurrent behavior with added Fe(III) redox shuttle (data reported here is light current density minus dark current density)







<u>William Gaieck</u> Materials Scientist (UCI Ph.D. Student)



Accomplishments: Reactor



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



<u>Kevin Tkacz</u> Materials Scientist (UCI Ph.D. Student)



Response to previous year reviewers' comments

"... it is unclear how much of the boost in efficiency and projected cost reduction can be attributed to the "new design" and how much would be attributed to having better-performing photocatalysts"

A techno-economic analysis using the H2A tool was conducted and it is clear that the new design saves significantly on cost, irrespective of the photocatalysts which are of course completely required for attaining this cost benefit.

"The funding of research on Type 2 PECs that is likely not to lead to a practical implementation is not advised. EERE is fully responsible for selecting projects based on real or anticipated contributions to achievable designs—those with the greatest potential for translation to practical applications."

Techno-economic analyses suggest that most PEC designs will not likely make a practical impact. The (new) Type 2 design is likely the most credible reactor design for practical PEC application.

"Project weaknesses include a lack of important understanding of particle stability, membrane integrity, and particle quantum yield."

In general, these are not within the proposed scope of work. Particle stability is a concern, but is a lesser concern given the poor quantum yields of particles to date. We are trying to understand the causes of these poor efficiencies and remedy them. Membrane integrity is not a concern; we have tested several filtration/osmosis membranes and they are all stable; the challenge is "baggie" transparency which we are exploring.

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 materials synthesis expertise (unfunded)

• Tokyo University of Science, Akihiko Kudo (Rh:SrTiO₃, BiVO₄)



Remaining Challenges and Barriers

Task 1.0 Numerical modeling and simulation of new reactor design

- Introduce complex fluid flow to enable simulation of forced convection, e.g. by electrolyte pumping.
- Introduce advanced optical phenomena to more accurately model E&M and particle photophysics.
- Introduce thermal effects to the full reactor model and investigate effects of natural convection.
- More accurately implement photocatalyst reactivity by modeling individual reactions on particles instead of baggie ensemble behavior as an ideal diode plus empirical Bulter–Volmer kinetics.

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

- 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 final deliverable.

<u>Final Deliverable</u>: Demonstrate > 3 standard L of H_2 (and > 1.5 L of O_2) from 8 hours of solar illumination.

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

Proposed Future Work

<u>Project Objective</u>: **Experimentally validate** a *new design* for scalable solar-H₂ technologies using laboratory-scale prototype particle suspension reactors

Description of Milestone – Solution Due Date (Quarter)
--

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 multiple physics	August 1, 2017 (Q8)	80%
by coding them into the current model and validating results		

Task 2.0 Experimental evaluation of chemicals, materials, and reactors

M2.3.2 Demonstrate > 1% η_{STH} in electrode form factor – Using thin-film and mesoporous electrodes, introduce electrocatalysts by photochemical deposition	May 1, 2017 (Q7)	25%
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, 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 rate of H_2 evolution	February 1, 2018 (Q10 / end)	15%

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

Project Summary

<u>Project Objective</u>: **Experimentally validate** a *new design* for scalable solar-H₂ 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, demonstrated stable operation of a tandem reactor operating at a 1% STH efficiency assuming most relevant physics. 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 , WO ₃ , or BiVO ₄ and for each of these, demonstrated photocurrent at a rate consistent with a 1% STH efficiency. Developed prototype reactors and techniques to locally assess redox shuttle concentration <i>in situ</i> .
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 1% STH efficiency.

Technical Backup Slides

Relevance: 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	← Half of this c to PVC pipe	ost is due s & pumps	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	Compressor	\$526 302						
subassembly	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 Baggies/piping Gas processing Control system	\$46 259 \$21 534 \$203 361 \$52 183	Excavation Baggies/piping Gas processing Control system	\$124 672 \$291 441 \$104 953 \$132 248	Panels/reactor Piping Gas processing Control system	\$1 076 962 \$30 843 \$243 743 \$95 959	Reactors Piping Gas processing Control system	\$746385 \$10521 \$2129 \$83932
Installation cost total	\$323 337		\$653 314		\$1 447 507		\$842 967	
Total capital cost with	\$1 393 822		\$2 343 728		\$11 028 052		\$4 291 722	
installation								

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

Prior Accomplishments: Materials



Houman Yaghoubi Electrical Engineer (UCI Postdoc)

Accomplishments: Rh:SrTiO₃ HER





- Electrons easily reduce Fe(III)
- Hole oxidation reactions of Fe(II) not noticeable

Fe(II) attenuates rate of Fe(III) oxidation for more selective reactivity

(XPS, UPS, SEM, EDS, XD, DRS, Raman, DLS)



Accomplishments: Separators



5		
1	50	
	BIL	

<u>Kevin Tkacz</u> 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

Accomplishments: In Situ EChem



Previously spatial spectroscopic probing, and now local electrochemical probing too





* During oxidation at WE(4), oxidative current at each UME drops off as the boundary/ diffusion layer grows

<u>William Gaieck</u> Materials Scientist (UCI Ph.D. Student)