# Tandem particle-slurry batch reactors for solar water splitting

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**Project ID # PD125**

# Overview

## Project Timeline

- Start date: July 1, 2015
- End date: June 30, 2017

## Budget

- Project funding: $1,248,063
  - Cost share: $ 254,304
  - DOE share: $ 993,759
- Projected funding by year
  - FY15/16: $ 685,210
  - FY16/17: $ 562,853

## Barriers Addressed

- Integrated Device Configurations
- Synthesis and Manufacturing
- Reactor Designs
- Auxiliary Materials

## Partners / Collaborators

- **Lawrence Berkeley National Laboratory & Joint Center for Artificial Photosynthesis, North** (Adam Weber): numerical device-physics modeling and simulation lead sub-recipient
- **California Institute of Technology & Joint Center for Artificial Photosynthesis, South** (Chengxiang Xiang): numerical device-physics modeling and simulation sub-contracted advisor
- **University of Tokyo** (Kazunari Domen) & **University of Houston** (Jiming Bao): particle materials advisors

# Relevance / Impact

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

2015–2016 Objective: Numerically demonstrate the feasibility of a reactor that exhibits a 1% solar-to-hydrogen (STH) conversion efficiency

| DOE Barriers and Targets | Project Goal |
| --- | --- |
| 2015 MYRD&D Targets for Solar $H_2$ Production using Particle Suspensions | • Demonstrate ≥ 1% STH efficiency for direct solar water splitting at $28.60/kg $H_2$ |
| AG) Integrated Device Configurations<br>AJ) Synthesis and Manufacturing | • Electrodeposit catalysts on light-absorber particles using bipolar electrochemistry, which is a scalable deposition method |
| AH) Reactor Designs | • Numerically model and simulate new designs for tandem two-vessel particle suspension reactors<br>• Fabricate and evaluate model reactors, and assess their transport capabilities |
| AI) Auxiliary Materials | • Identify the most efficient redox shuttles based on rates of mass transport and rates of electrocatalysis |

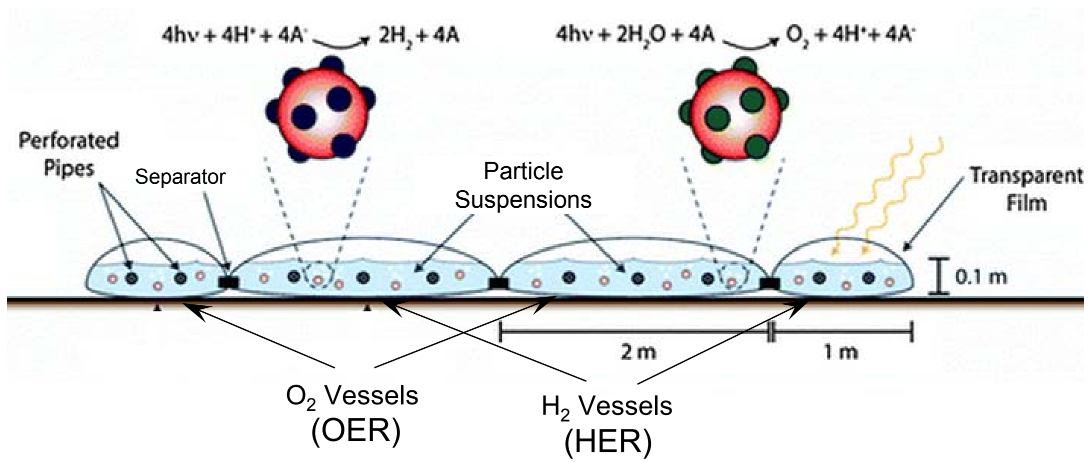
# Approach

## Proposed New Reactor Design

**Conventional Design**

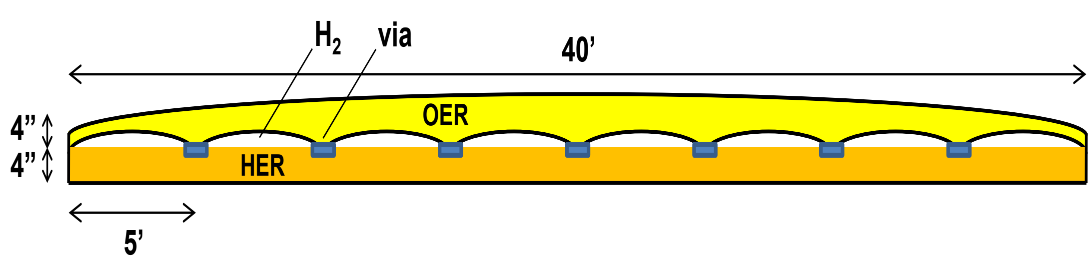
Solar water splitting reactor consisting of two particle suspensions arranged side-by-side and connected by a porous via to allow mixing of the molecular redox shuttle (A/A⁻).

*Limitation*: Large mass transport distances for A/A⁻ and no STH efficiency benefit for the tandem design.




**Proposed Design**

Stacked vessels afford short mass transport distances for A/A⁻ and a ~50% increase in the maximum theoretical STH conversion efficiency.



# Approach

## High-Level Structure

| Task | Subtask |
| --- | --- |
| **(T1.0)** Numerical Modeling and Simulation | **(S1.1)** Vertically stacked reactor designs<br>**(S1.2)** Electrochemical techniques<br>**(S1.3)** Reactor optimization |
| **(T2.0)** Experimental Evaluation of Chemicals, Materials, and Reactors | **(S2.1)** Experimental electrochemical apparatus<br>**(S2.2)** Redox shuttle characterization<br>**(S2.3)** Particle synthesis and characterization<br>**(S2.4)** Model reactor fabrication and evaluation |

# Milestones (Year 1)

## Quarter 1 (of 8): July – September, 2015

| Description of Milestones | Verification Process |
| --- | --- |
| **(M1.1.1)** A functioning and converging reactor *model* for the proposed tandem dual-compartment particle suspension reactor, which accounts for coupled charge transport, fluid flow, and electrochemical reactions via Butler–Volmer kinetics. | Basic designs will be evaluated and basic model variables will be varied to determine which result in the largest STH efficiencies. |

## Quarter 3 (of 8): January – March, 2016

| Description of Milestones | Verification Process |
| --- | --- |
| **(M2.2.2)** A functioning basic reactor, according to details in M1.1.1, and evaluation of redox shuttle transport. | Mass-transport-limited-current measurements and open-circuit-potential measurements will be conducted to verify that a 1% STH efficiency reactor is feasible during prolonged operation. |

# Milestones (Year 1)

## Quarter 2 (of 8): October – December, 2015

| Description of Milestones | Verification Process |
| --- | --- |
| **(M1.2.1)** A functioning and converging *model* for a particle evaluation apparatus and an electrocatalyst deposition apparatus using bipolar electrochemistry, which includes variables of system dimensions, particle dimensions, catalytic properties, and electrolyte conductivity. | Experiments and numerical simulations will be quantitatively compared for basic electrochemical designs to determine which result in the most selective catalyst deposition. |
| **(M2.1.1)** A functioning and converging particle evaluation apparatus and electrocatalyst deposition apparatus using bipolar electrochemistry. | Deposition of state-of-the-art electrocatalysts on model $TiO_2$ particles using bipolar electrochemistry and verification using standard materials characterization techniques. Also, measurement of current–potential behavior of particles using bipolar electrochemistry. |
| **(M2.2.1)** Identification of the most efficient multiple-electron-transfer redox shuttles in comparison to one-electron-transfer redox shuttles. | Redox shuttle optical properties and concentrations will be evaluated using ultraviolet–visible absorption spectroscopy, and catalytic properties and diffusion coefficients will be evaluated using electrochemistry at carbon electrodes to identify those with the smallest absorptivity and most rapid catalysis and diffusion, which manifest into the largest STH efficiency. |

# Milestones (Year 1)

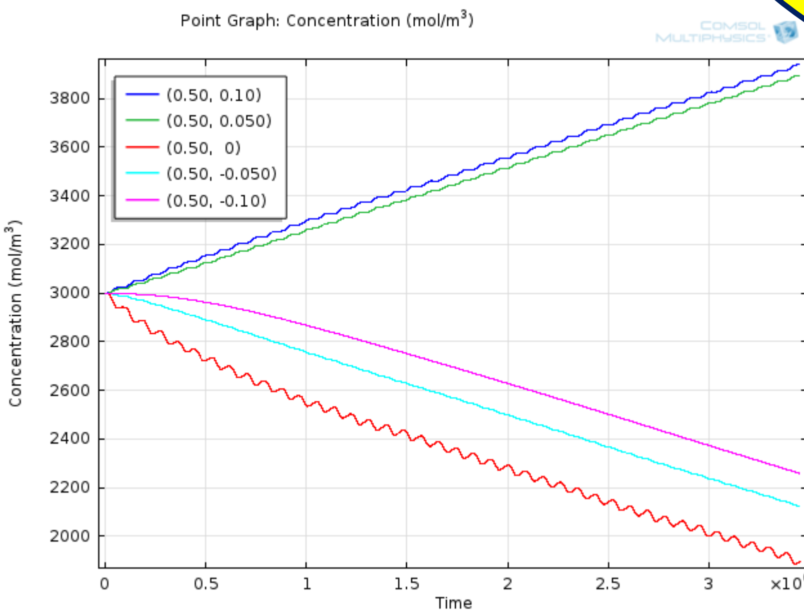
## Quarter 4 (of 8): April – June, 2016

| Description of Milestones | Verification Process |
| --- | --- |
| **(M1.1.2)** A functioning and converging reactor *model* that includes advanced semiconductor charge transport, including generation and recombination phenomena for bulk and surface recombination. | Kinetic rate constants and/or lifetimes of several semiconductor materials, e.g. Si and GaAs, will be input into the models to verify that current–voltage behavior at electrodes made of these materials (from the literature) will be translated to the particle suspensions, when surface recombination is not limiting. |
| **(D1.1.1) A vertically stacked reactor *model* based on parameters in the 2009 techno-economic analysis (e.g. height of vessels, etc.) that is numerically simulated to be capable of attaining a 1% STH efficiency with 80% less pipes and 80% less pumping energy than modeled for similar Type 2 reactors analyzed in the techno-economic analysis performed by Directed Technologies, Inc. for the US DOE.** | **A steady-state concentration of redox shuttle between the vessels which does not result in a loss of more than 120 mV due to redox shuttle concentration gradients after one year of simulated operation using actual solar irradiance data.** |

# Accomplishments / Progress

Quarter 3/4

Quarter 3/4


- Model tandem reactor with porous via
  - Simulated sunlight irradiance
  - Beer–Lambert law absorption in each vessel
  - $H_2$ rate consistent with 1% STH efficiency; photovoltage not considered

- Model preliminary results
  - Iodide concentration over 40 days; legend indicates (*x*, *y*) position
  - Triiodide concentration changes (not shown) are opposite and 3x smaller
  - Max. Nernst potential loss is ~13 mV

**Numerical models support the feasibility of the reactor design**

# Collaborations

- Lawrence Berkeley National Laboratory (Federal Lab) & Joint Center for Artificial Photosynthesis (DOE Hub) (Adam Weber; sub)
  - » Core numerical device physics modeling and simulation effort, specifically multi-physics and chemical engineering
- California Institute of Technology (University) & Joint Center for Artificial Photosynthesis (DOE Hub) (Chengxiang Xiang; sub)
  - » Additional expertise in numerical device physics modeling and simulation, specifically ray tracing and semiconductor physics
- University of Tokyo (University; Kazunari Domen; unfunded)
  - » Expertise in particle materials synthesis
- University of Houston (University; Jiming Bao; unfunded)
  - » Expertise in particle materials synthesis

# Proposed Future Work

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

2015–2016 Objective: Numerically demonstrate the feasibility of a reactor that exhibits a 1% solar-to-hydrogen conversion efficiency

2016–2017 Objective: Experimentally demonstrate > 3 standard liters of $H_2$ from a ~12" x ~12" laboratory-scale particle suspension reactor over 8 hours of continuous operation under sunlight illumination

## Quarter 5 (of 8): July – September, 2016

| Description of Milestones | Verification Process |
| --- | --- |
| **(M2.3.1)** Synthesis and characterization of as many of the following materials as possible: CoO, $ZrO_2$-TaON, $BiVO_4$, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$, $SrTiO_3$:Rh, and $WO_3$ nanometer-to-micron-sized particles, with and without deposited electrocatalysts. | The following properties will be determined: crystallinity, bandgap energy, band-edge positions, doping density, and photoelectrochemical performance in electrode form factor and particle form factor. |

# Proposed Future Work

## Quarter 6 (of 8): October – December, 2016

| Description of Milestones | Verification Process |
|---|---|
| **(M2.3.2)** Evaluation of the champion materials from M2.3.1 toward the 2015 MYRD&D technical targets. | Using a light source and the reactor from M2.2.2, the particle lifetime and performance will be evaluated through analysis of reaction products by ultraviolet–visible absorption spectroscopy and/or mass spectrometry, and subsequent calculation of quantum yields. |

## Quarter 7 (of 8): January – March, 2017

| Description of Milestones | Verification Process |
|---|---|
| **(M1.1.3)** A functioning and converging reactor *model* that includes additional relevant physics such as electromagnetic wave propagation, thermal effects, and multi-phase flow phenomena, and which are then used to determine optimal particle size and reactor shape, effects due to variations in temperature, and properties that result in safe operating conditions in terms of crossover (< 4% $H_2$ in $O_2$). | Known temperature-dependent properties for the electrolyte and the materials, e.g. Si, GaAs, and electrocatalysts, will be input into the models to verify that these properties for solutions and wafers (from the literature) will be translated to the particle suspensions and that rates of $H_2$ crossover and overall efficiency compare with empirical results. |

# Proposed Future Work

## Quarter 8 (of 8): April – June, 2017

| Description of Milestones | Verification Process |
|---|---|
| **(M1.3.1)** An optimized reactor design based on numerical *model* sensitivity and parameter analyses. | Reactor designs will be numerically modeled, simulated, and compared for their STH efficiency to determine the most efficient designs. |
| **(M2.4.1)** Demonstration of enhanced stability, catalytic activity, and overall STH efficiency for the champion materials and reactor from M2.3.1 and M2.2.2. | Using additional techniques (e.g. real-time mass spectrometry, transient-absorption spectroscopy, time-resolved microwave conductivity, bipolar electrochemistry), particles will be evaluated and modified for a 1% STH efficiency and large open-circuit photovoltage. |
| **(M2.4.2)** Advanced model reactors, designed and fabricated according to details from M1.3.1. | State-of-the-art particles from M2.4.1 will be evaluated in several reactor designs to verify that the new design results in a more efficient and less expensive reactor. |
| **(M2.4.3)** Demonstration of > 3 standard liters of $H_2$ from 8 hours of continuous operation under sunlight illumination for a ~12" x ~12" reactor containing particles from M2.4.1 and a reactor from M2.4.2. | Using simulated sunlight illumination, the particle performance target will be evaluated through analysis of reaction products by ultraviolet–visible absorption spectroscopy, mass spectrometry, and/or gas chromatography. |

# Project Summary

**Demonstration of a scalable and cost-effective laboratory-scale particle suspension reactor for solar hydrogen production**

| DOE Barriers and Targets | Project Goal |
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| 2015 MYRD&D Targets for Solar $H_2$ Production using Particle Suspensions | • Demonstrate ≥ 1% STH efficiency for direct solar water splitting at $28.60/kg $H_2$ |
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