II.D.3 Tandem Particle-Slurry Batch Reactors for Solar Water Splitting

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Project Start Date: August 1, 2015
Project End Date: January 31, 2018 (including a 6-month no cost extension)

Overall Objectives

- Experimentally validate a benchtop-scale tandem particle-slurry batch reactor as a scalable technology for solar hydrogen production at a projected cost of ≤$20.00 per gallon of gasoline equivalent.
- Demonstrate a ~12 in x 12 in model reactor that generates H_2 at a rate of >3 L per 8 h of solar illumination.

Fiscal Year (FY) 2017 Objectives

- Incorporate into the numerical reactor model more accurate physics for electromagnetic wave propagation, thermal effects, and gas crossover.
- Experimentally demonstrate two particle materials that together exhibit a 1% solar-to-hydrogen (STH) efficiency in electrode form factor.
- Experimentally demonstrate the feasibility of a reactor that exhibits a 1% STH efficiency while using at least 80% less pipes and 80% less energy required to pump and circulate the electrolyte than modeled for similar reactors analyzed in the 2009 techno-economic analysis [1,2].

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan.

(AG) Integrated Device Configurations

(AH) Reactor Designs

(AI) Auxiliary Materials

(AJ) Synthesis and Manufacturing

Technical Targets

This project is conducting experimental studies and numerical modeling and simulations of a new tandem particle-slurry batch reactor design for solar water splitting that uses photocatalyst semiconductor particle suspensions and consists of two stacked compartments. Insights gained from these studies will be applied toward the design of plant-scale reactors to meet the following DOE hydrogen production targets for dual-bed photocatalyst reactors.

- Cost: ≤$20.00/kg H_2
- STH Energy Conversion Ratio: ≥1% and >3 L H_2 per 8 h of solar illumination

FY 2017 Accomplishments

- Performed techno-economic analyses; the results suggest that our stacked-bed reactor design can generate H_2 at a cost that meets the ultimate DOE target of <$2/kg H_2 for a ~8.5% STH efficient reactor; the side-by-side-reactor design required a ~14.5% STH efficient reactor to achieve this cost.
- Demonstrated *in silico* that a stacked-bed reactor can sustain indefinite operation at 3.8% STH efficiency under diurnal excitation conditions using photocatalyst particles with bandgaps based on state-of-the-art materials (Rh-modified $SrTiO_3$ and $BiVO_4$), concentrations of the IO_3^-/I^- redox shuttle within their solubility ranges, and membrane permeability such that gas crossover remains below the explosive limit.
- Demonstrated that several small-scale prototype reactors containing aqueous photocatalyst particle suspensions can drive H_2 evolution.

INTRODUCTION

Economically, particle slurry reactors are projected to be one of the most promising technologies for clean solar photoelectrochemical hydrogen production via water splitting, according to a 2009 techno-economic analysis commissioned by the DOE and performed by Directed Technologies, Inc. [1,2]. This techno-economic analysis compared four plausible reactor designs: two panel-based reactors, which resembled typical wafer-based solar cells immersed in a liquid electrolyte, and two particle-slurry reactors. On an energy basis, the hydrogen produced from the particle-slurry reactors was projected to be by far the most cost-competitive with fossil fuels, further supporting the viability of the hydrogen economy. This project describes a new design for a particle-slurry reactor, where the main innovation is the use of a stacked-compartment arrangement, instead of the typical design where the compartments are arranged side-by-side (Figure 1a). By stacking the compartments, which results in much shorter mass transport distances and provides efficiency advantages due to the tandem light absorbers, it is projected that over five times less piping and pumps are required to circulate the electrolyte, which results in a cost that is half that of the least expensive proposed particle-slurry reactors to date (Figure 1b).

As part of the proposed work plan, the device physics of the reactor designs were numerically modeled and simulated, and it was determined that in the absence of piping and pumps, a 3.8% STH efficient reactor could operate indefinitely, for compartments that are each 1 cm tall, and including absorption by soluble state-of-the-art particles present at ideal particle concentrations and the common IO_3^-/I^- redox shuttle below its aqueous solubility limit. It was also determined that photocatalyst particles with smaller bandgap energies could drive a sustainable reactor using our design at a 10% STH efficiency. These results are significant because achieving the 3.8% STH efficiency metric would meet the 2015 MYRDD Plan targets, while demonstrating the 10% STH efficiency metric with inexpensive particle materials would meet the ultimate MYRDD Plan target. We have also fabricated and tested small-scale experimental prototypes to aid in numerical model validation and to isolate the effects of underlying physical phenomena on the overall reactor performance. By direct mass spectroscopic detection, we have observed H_2 evolution during illumination of photocatalyst particle suspensions. Eventually, we will leverage the numerical model and small-scale prototypes to experimentally evaluate a benchtop-scale (12 in x 12 in) reactor prototype. Toward this, we have synthesized several state-of-the-art semiconductor nanoparticle photocatalysts and evaluated them experimentally: Rh-modified $SrTiO_3$, $BiVO_4$, and WO_3 [3].

APPROACH

The overarching approach to achieving the objectives of the project was to combine theoretical and numerical modeling efforts with experimental measurements to design and optimize reactor performance. Simulation results were used to evaluate the feasibility of various reactor parameters, including overall design and dimensions of the reactor, properties and characteristics of the semiconductors and electrocatalysts, and concentration of redox-active electrolyte. This information was then used to synthesize state-of-the-art materials, characterize and engineer their relevant properties, and evaluate their overall efficacy in prototype reactors for solar hydrogen production. In general, the numerical and experimental data sets were in good agreement, therefore validating this choice of physical phenomena and equations used in the simulations. Discrepancies between theory and experiments were used to fine-tune each via a checks-and-balances process.

RESULTS

The numerical model was used to evaluate the reactor size and concentrations of semiconductor particle and redox shuttle that would enable at least a 1% STH efficiency,

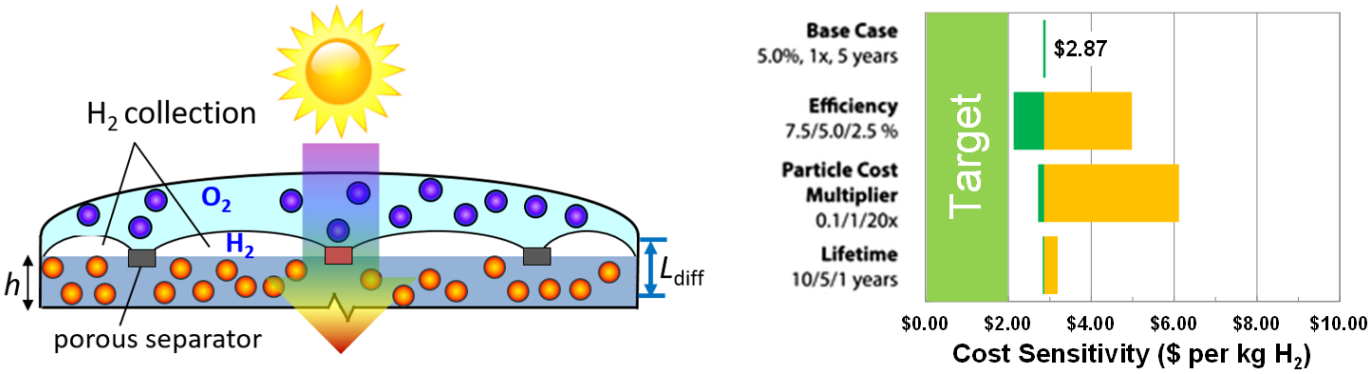


FIGURE 1. (a) Schematic of the vertically stacked particle-suspension reactor design which affords tandem light absorption for Z-scheme solar water splitting. (b) Results from a techno-economic analysis and sensitivity analyses performed using the DOE H2A tool for hydrogen production using a Type 2 reactor design (https://www.hydrogen.energy.gov/h2a_production.html) [1,2].

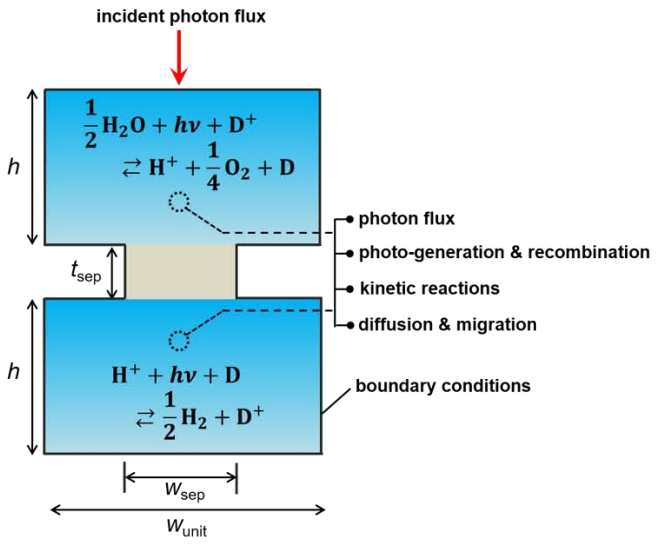
consistent with the prior go/no-go decision. While the go/no-go decision required modeling 10 cm tall reactor compartments, which are consistent with the heights modeled in prior techno-economic analyses of similar reactor designs [1,2], this is not a strict functional requirement for these reactors, so intermediate compartment heights down to 1 cm each were considered. The main physical processes incorporated into the model are shown in Figure 2a.

From the standpoint of designing a reactor to operate sustainably with only passive diffusion facilitating mass transport, the main factors we considered were the diffusivity and aqueous solubility of the redox shuttle and the tradeoffs in increasing the redox shuttle concentration on competitive light absorption. Based on reported data in the literature, iodine-based and iron-based redox shuttles (I_3^-/I^-, IO_3^-/I^-, and Fe^{3+}/Fe^{2+}) have been used in the most efficient tandem particle suspensions [3]. However, at the estimated minimum species concentrations needed to sustain indefinite reactor operation, i.e., 0.1–2.5 M, only the proton-coupled electron-transfer redox shuttle IO_3^-/I^- transmitted sufficient light to enable efficient operation. Model results indicated that for 1 cm tall compartments and concentrations of the redox shuttle that were less than the solubility limit (~0.4 M), a reactor operating at a 3.8% STH efficiency would reach approximate steady-periodic operating conditions in about three days (Figure 2b). *These results are important to achieving the DOE MYRDD Plan targets because they demonstrate the validity of the reactor design for a >1% STH efficient system with no physical limitations to infinitely long-term operation.*

Other physical processes that are being explored outside of the main inclusive modeling framework are effects of light scattering and thermal transport, including natural convection. In order to validate the computational approaches, model experiments using small-scale prototypes are being performed.

Figure 3 shows the overall small-scale prototype setup and gas flow diagram including mass spectrometric gas detection during photocatalytic H_2 evolution from particle suspensions. Also shown is a photograph of the small-scale reactor and data obtained using this experimental setup for Rh-modified $SrTiO_3$ particles at varying concentrations of each half of the iron aquo redox shuttle. The detection system relies on atmospheric pressure inline gas detection with an argon carrier gas and has a ~10 second detection limit. These are the first quantitative results obtained using this reactor and gas detection system and are important to achieving DOE targets because they demonstrate that a two-particle tandem particle-slurry reactor is regenerative and can evolve H_2 upon simulated solar illumination. Notably, the quantum yield for H_2 increased as the concentration of Fe(II) increased, likely because Fe(II) is required to regenerate the initial state of the photocatalyst particles during H_2 evolution. Conversely, the quantum yield for H_2 decreased as the concentration of Fe(III) increased, likely because Fe(III) competes with protons for reduction by photogenerated electrons in the photocatalyst particles.

Figure 4 shows design drawings and digital photographs of the larger-scale prototype reactor with two cubic compartments, each 1 L in volume, and a height dimension that can be easily adjusted. A slightly larger version of this reactor will be used to assess the ultimate project goal in terms of STH efficiency and long-term on-sun studies. These results are important to achieving DOE targets because they



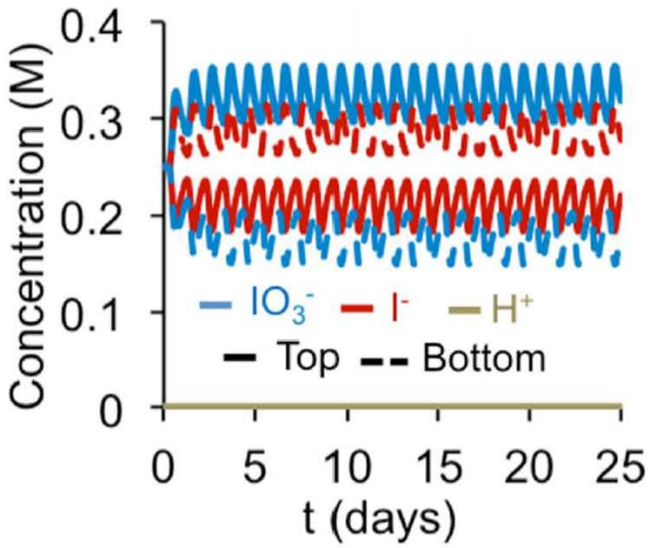


FIGURE 2. (a) Numerical device physics modeling domain for the concept shown in Figure 1a indicating the major physical processes that are incorporated into the model. (b) Average redox shuttle concentrations in each compartment as a function of time, for 1 cm tall compartments containing the IO_3^-/I^- redox shuttle (initially 0.25 M of each species) and Rh-modified $SrTiO_3$ (top, hydrogen evolution reaction [HER], 3.3×10^{-3} g L^{-1}) and $BiVO_4$ (bottom, oxygen evolution reaction [OER], 3.7×10^{-3} g L^{-1}) operating at a 3.8% STH efficiency.

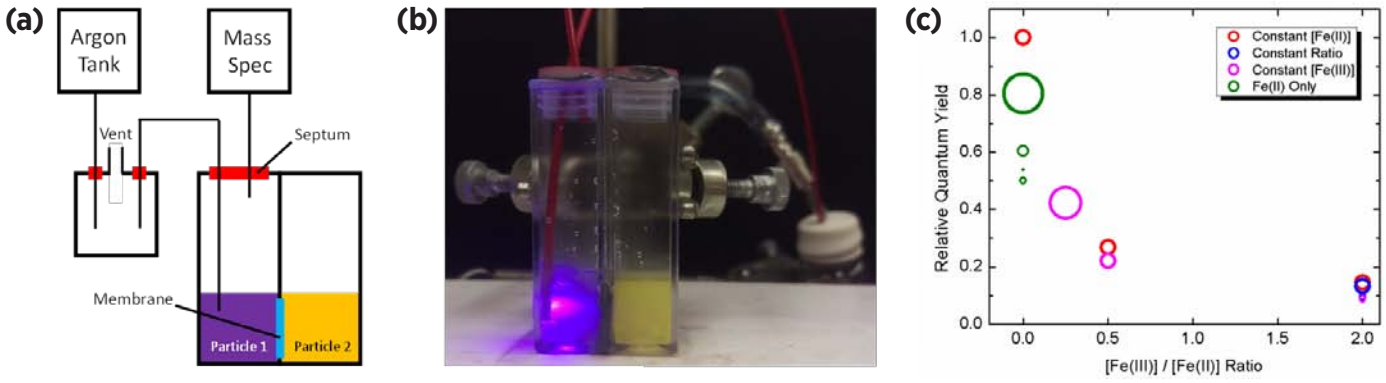


FIGURE 3. (a) Scheme and (b) digital photograph of a thin-pathlength particle suspension reactor prototype made of quartz and containing particles of Rh-modified $SrTiO_3$ in the left compartment and particles of $BiVO_4$ in the right compartment, with an intervening dialysis membrane. Optical illumination using 405 nm light was incident from the left side onto the Rh-modified $SrTiO_3$ compartment, and shown is tubing for gas flow from an Ar tank through the rapidly stirred Rh:$SrTiO_3$ compartment and to a mass spectrometer. (c) Relative quantum yield of H_2 detected by mass spectrometry during illumination of a suspension of Rh-modified $SrTiO_3$ particles with 405 nm laser light and containing a varied concentration of the Fe(II) aquo redox shuttle (ranging from 2 mM to 50 mM, denoted by marker size) and a varied Fe(III):Fe(II) ratio. Each color represents one series of experiments where only one parameter was varied. The relative size of each data point represents the concentration of Fe(II) used. Some decrease in the signal over time for the experiments containing Fe(II) only was attributed to aggregation of the particles on the sides of cuvette.

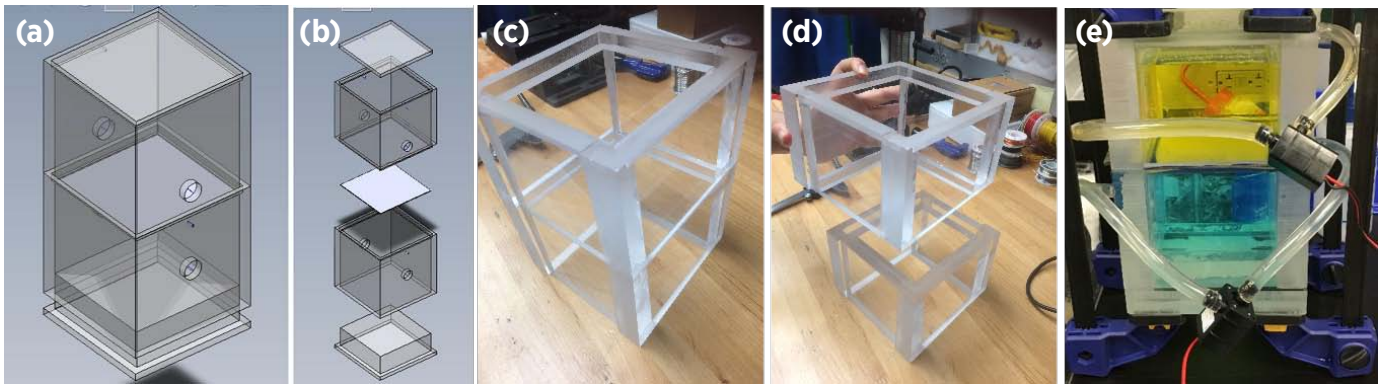


FIGURE 4. (a,b) Computer-aided design drawings and (c,d,e) digital photographs of a particle suspension reactor prototype containing dye solutions in each compartment to highlight the geometry and slow diffusive flux through a nanoporous separator. Each reactor compartment is 4 in x 4 in x 4 in, contains an adjustable borosilicate glass window on the top of the reactor, contains custom Viton seals between the top and bottom compartments to attenuate leaking, and enables forced convection through active pumping circulation of the electrolyte.

demonstrate that a reactor of near complete size exists to measure the ultimate milestone and project target of this work.

CONCLUSIONS AND UPCOMING ACTIVITIES

Numerical models, simulations, and techno-economic analyses suggest that a dual bed reactor consisting of stacked compartments and no convection can achieve at least a 1% STH efficiency and as much as a 10% STH efficiency when 1 cm tall reactor compartments and the appropriate redox shuttle are utilized. Benchtop-scale reactors have been built and H_2 has been detected from smaller-scale reactors using a new mass spectrometric detection system. Ultimately, the proposed photocatalyst particles, cocatalysts, and redox shuttles will be assessed using benchtop-scale prototypes with ~12 in x 12 in illumination areas and with a target of generating >3 L of H_2 per 8 h of solar illumination. No additional work beyond this project is likely, but open issues remain, including photocatalyst particle size effects on individual particle physics and reactivity, effects of optical scattering and thermal natural convection, optimization of photocatalyst particle performance with and without cocatalysts, and design rules for efficient photocatalyst particles.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. R. Bala Chandran, S. Breen, Y. Shao, S. Ardo, A.Z. Weber, *Energy Environ. Sci.*, 2017, *Advance Article,* DOI: 10.1039/C7EE01360D, "Evaluating particle-suspension reactor designs for Z-scheme solar water splitting *via* transport and kinetic modeling."

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3. S. Ardo, *U.S. DOE EERE FCTO Annual Merit Review,* **June 2017**, Washington, DC, "Tandem particle-slurry batch reactors for solar water splitting."

4. W. Gaieck, K. Tkacz, C.D. Sanborn, Y. Shao, S. Breen, H. Yaghoubi, R. Bala Chandran, A.Z. Weber, S. Ardo, *231st Electrochemical Society Spring National Meeting*, **May 2017**, New Orleans, LA, *(Invited)* "Recent Progress in Fundamental Photoelectrochemical Studies Relevant to New Low-Cost Designs for Z-Scheme Solar Water Splitting Reactors."

5. R. Bala Chandran, L.-C. Weng, S. Ardo, A.T. Bell, A.Z. Weber, *231st Electrochemical Society Spring National Meeting*, **May 2017**, New Orleans, LA, *(Invited)* "Mathematical Modeling of Novel Artificial-Photosynthesis Devices."

6. R. Bala Chandran, S. Ardo, A.Z. Weber, *2016 Materials Research Society Fall National Meeting & Exhibit*, **December 2016**, Boston, MA, "Modeling Transport and Interfacial Effects in a Particle-Suspension Reactor for Solar Water Splitting."

7. W. Gaieck, K. Tkacz, C.D. Sanborn, Y. Shao, S. Breen, R. Bala Chandran, H. Yaghoubi, C. Xiang, A.Z. Weber, S. Ardo. *2016 American Institute of Chemical Engineers Fall National Meeting*, **November 2016**, San Francisco, CA, *(Invited; Plenary)* "Photocatalysis for Z-Scheme Solar Water Splitting Using New Reactor Designs."

8. W. Gaieck, K. Tkacz, C.D. Sanborn, Y. Shao, S. Breen, R. Bala Chandran, H. Yaghoubi, C. Xiang, A.Z. Weber, S. Ardo. *2016 Pacific Rim Meeting (PRiME) on Electrochemical and Solid-State Science, Joint International Meeting of the Electrochemical Society of the United States of America and Japan,* **October 2016**, Honolulu, HI, *(Invited)* "New Reactor Designs for Z-Scheme Solar Water Splitting Photocatalysis."

9. K. Tkacz, C.D. Sanborn, S. Ardo. *Pacific Rim Meeting (PRiME) on Electrochemical and Solid-State Science, Joint International Meeting of the Electrochemical Society of the United States of America and Japan*, **October 2016**, Honolulu, HI, "Photoelectrochemical Evaluation of Single Nanoparticles."

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