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

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Project End Date: July 31, 2017

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-inch by ~12-inch model reactor that generates H_2 at a rate of >3 L per 8 hours of solar illumination.

Fiscal Year (FY) 2016 Objectives

- Using numerical simulations, demonstrate the feasibility of a reactor that exhibits a 1% solar-to-hydrogen (STH) conversion efficiency while using at least 80% less pipes and energy required to pump and circulate the electrolyte than modeled for similar reactors analyzed in the 2009 techno-economic analysis.

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 Plan.

(AG) Integrated Device Configurations

(AH) Reactor Designs

(AI) Auxiliary Materials

(AJ) Synthesis and Manufacturing

Technical Targets

This project entails combined numerical modeling, simulations, and experimental studies related to a new tandem particle-slurry batch reactor design for solar water splitting using photocatalyst semiconductor particle suspensions and consisting 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 systems.

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

FY 2016 Accomplishments

- Demonstrated in silico that a 1% STH efficient dual bed reactor can satisfy the go/no-go decision and the 2015 DOE Multi-Year Research, Development, and Demonstration Plan STH efficiency target.
- Demonstrated that a combination of two particle electrodes can attain the voltage required to split water.
- Developed several small-scale reactors of varying sizes in order to assess the validity of the numerical models and to serve as benchtop-scale prototypes.

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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 U.S. Department of Energy 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. 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 pipes and pumping energy are required to circulate the electrolyte, which results in a lower plant cost than that of the least expensive proposed particle-slurry reactors to date.

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 1% STH efficient reactor with specific particle concentrations and redox shuttles could continuously operate for over one year and therefore, essentially operate indefinitely. This is significant because it satisfies our go/no-go decision and suggests that the 2015 DOE Multi-Year Research, Development, and Demonstration Plan targets can be met with this significantly less expensive design. We have also begun fabricating and testing small-scale experimental prototypes to aid in numerical model validation and to isolate the effects of underlying physical phenomena on the overall reactor performance. Eventually, we will leverage the numerical model and small-scale prototypes to fabricate a benchtop-scale (12-inch by 12-inch) reactor prototype that will be evaluated experimentally. Toward this, we have synthesized several state-of-the-art semiconductor particle materials, and, using electrodes cast from state-of-the-art Rh-modified $SrTiO_3$ nanoparticles and $BiVO_4$ nanoparticles, we have demonstrated that together they can generate the photovoltage required to split water. We have also demonstrated bipolar electrodeposition of electrocatalysts on model spherical carbon particles, hundreds of microns in size, and measured a photovoltage response from one-to-few TiO_2 nanoparticles covalently attached to a single nanopore in a poly(ethylene terephthalate) thin film when wetted on both sides by electrolyte, indicative of interfacial electronic charging and photovoltaic behavior. These contactless techniques for depositing materials and measuring performance of nanoparticles afford in situ and in operando fabrication and characterization abilities.

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 optimal semiconductor particle concentrations, redox shuttle concentrations, and reactor heights to attain desired reactor performance.

The numerical model is transient, two-dimensional, and implemented in COMSOL multiphysics simulation software. The modeling domain is shown in Figure 1. The model included the following relevant physics:

- Gaussian diurnal illumination cycles to mimic solar illumination.
- Optical absorption that follows the Beer–Bouger–Lambert law.
- Competitive light absorption by the redox shuttle.
- A photodiode as the power supply driven by the input sunlight.
- Butler–Volmer reaction kinetics for state-of-the-art oxygen-evolving electrocatalysts and hydrogen-evolving electrocatalysts, but with equal charge-transfer coefficients to expedite implementation.
- Volumetric reaction rates, instead of areal current densities, to represent solution redox chemistries.
- Species transport due to diffusive and migratory fluxes.
- Effects of the separator porosity on species diffusivities
- Optional daily recirculation of the electrolyte between the compartments.

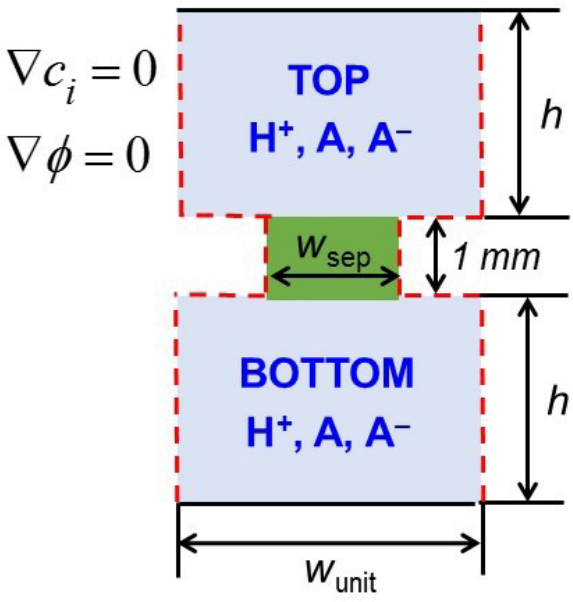


FIGURE 1. Numerical device physics modeling domain under periodic boundary conditions for a tandem stacked-compartment particle-slurry reactor, where each reactor is of height, h, and contains regularly spaced and sized separators of width, w_{sep}, per width of the reactor, w_{unit}. The aqueous electrolyte solutions in each reactor include protons (H^+), oxidized and reduced versions of the redox shuttle (A/A^-), and counterions.

- Counterions for the redox shuttle, other than protons.
- Dissolved gas transport to optimize the size of the porous separator.

In order to validate the computational approach, small-scale experimental prototypes were also developed. For example, the use of Fickian diffusion to model solution species transport behavior was validated experimentally using a rectangular electrochemical cell filled with an aqueous solution of electrolyte redox shuttle. The absorbance was monitored spectroscopically at a fixed position from an electrode biased to drive solution redox chemistry to evaluate transient concentration profiles. The numerical and experimental data sets were in good agreement, therefore validating the physics. Discrepancies between theory and experiments were used to fine-tune both via feedback loops. This process afforded checks and balances to the work in order to minimize time spent on a specific task or aspect of the project that was unlikely to succeed.

RESULTS

The numerical model was used to optimize the reactor size and semiconductor particle and redox shuttle concentrations to achieve at least 1% STH efficiency, consistent with the go/no-go decision. We focus here on presenting the case using 10-cm-tall compartments, which are consistent with the heights modeled in prior techno-economic analyses of similar reactor designs.

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^- and Fe^{3+}/Fe^{2+}) have been used in the most efficient tandem particle suspensions. However, at the estimated minimum species concentrations needed to sustain indefinite reactor operation, i.e., 1–2.5 M, these redox shuttles substantially absorb visible light, therefore greatly attenuating absorption by the particles. Model results indicated that for 10-cm-tall compartments, concentrations less than 1 mM were required in order to generate rates of hydrogen evolution consistent with a 1% STH efficiency.

Therefore, we considered organic redox shuttles, such as quinones, as alternatives in order to reduce the extent of light absorption and to utilize the added benefit of proton-coupled electron transfer that can enable sustained reactor operation at near-neutral pH, i.e., pH ≈ 7 (~10^{-7} M H^+). By coupling electron transfer and proton transfer reactions, concomitant with H_2 evolution or O_2 evolution reactions, no net protons are liberated or consumed and, therefore, small concentrations of protons, e.g., 10^{-7} M, can be maintained during operation. Model results for the average concentration profiles of the redox shuttle, initially present as 1 M *para*-benzoquinone (Q), 1 M hydroquinone (QH_2), and 10^{-3} M protons (H^+), are shown in Figure 2a. These simulations assumed 10-cm-tall compartments with particle concentrations of 0.0013 g/L $BiVO_4$ in the top compartment and 1.7 g/L Rh-modified $SrTiO_3$ in the bottom compartment. The reactor attained approximate steady-periodic operating conditions after 200 days, at which time each compartment operated at a projected current density of ~0.85 mA/cm^2, a rate consistent with a 1% STH efficiency. Even though the Q/QH_2 redox shuttle has an aqueous solubility less than 0.6 M, higher solubilities exist when Q/QH_2 is modified with sulfonate groups [3]. Therefore, we have demonstrated that the proposed design can operate safely and sustainably with only diffusive mass transport in the absence of any pumps or piping infrastructure. Figure 2b depicts the time

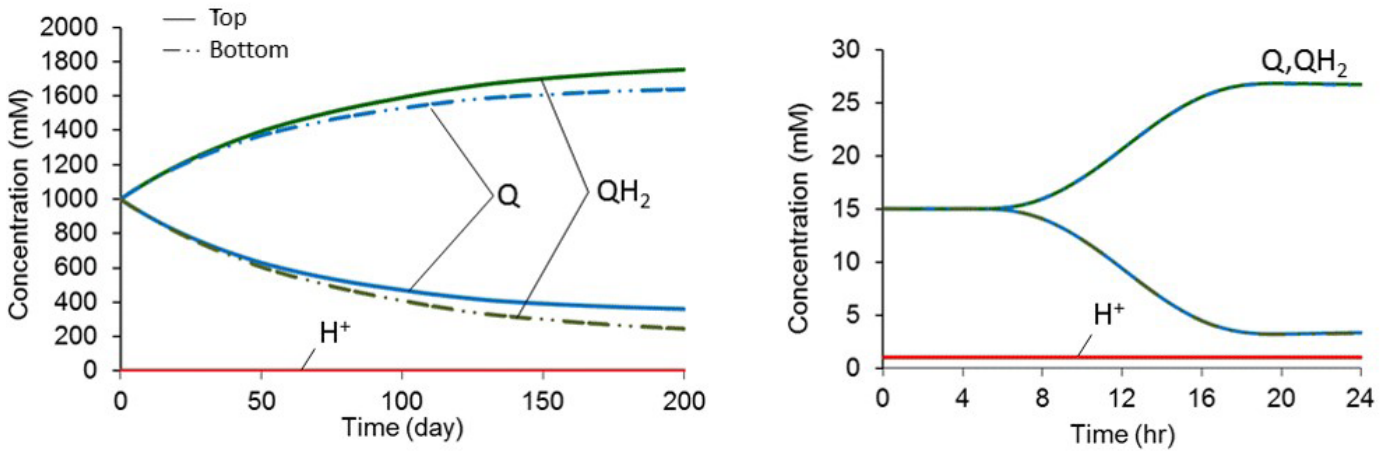


FIGURE 2. Species concentration profiles of *para*-benzoquinone (Q), hydroquinone (QH_2), and protons (H^+) for compartments each 10-cm tall containing 0.0013 g/L $BiVO_4$ in the top compartment and 1.7 g/L $SrTiO_3$:Rh in the bottom compartment with initial pH of 3 and Q/QH_2 concentrations of (a) 1 M and (b) 15 mM

evolution of species concentration for reactor operation over one day, suggesting that even at 15 mM Q/QH_2, the reactor can operate at a 1% STH efficiency. Based on our calculations, operating the pumps for one hour every night, and decreasing the amount of pipes by ~90%, provides convective recirculation and stirring sufficient to homogenize the reactor contents. This process is expected to consume less than 0.03 kW, which is an 85% reduction from the pumping power estimated in prior techno-economic analyses of similar reactor designs. Modeling results therefore suggest a reasonable potential toward sustainably operating a 1% STH efficient prototype tandem particle-slurry batch reactor for close to one year in 10-cm-tall reactor compartments, consistent with meeting the go/no-go decision. These results are important to achieving the DOE Multi-Year Research, Development, and Demonstration Plan targets because they demonstrate the validity of the reactor design for a 1% STH efficient system.

Figure 3 shows experiment results from photoelectrochemical measurements with electrodes made from Rh-modified $SrTiO_3$ and $BiVO_4$. These data indicate that together these two materials can generate the voltage required to split water, a process that requires at least 1.23 V of potential at standard state. While the electrolytes used were at different pH values, these data suggest that these materials, or closely related materials, are likely the best combination to drive overall solar water splitting. These results are important to achieving DOE targets because they demonstrate that a two-particle tandem particle-slurry reactor could split water using sunlight.

Figure 4 shows the open-circuit photovoltage over time that resulted from illumination of a single nanopore in

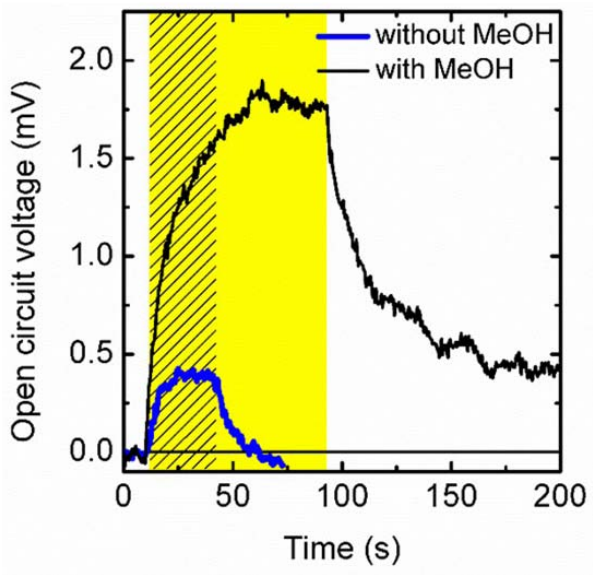
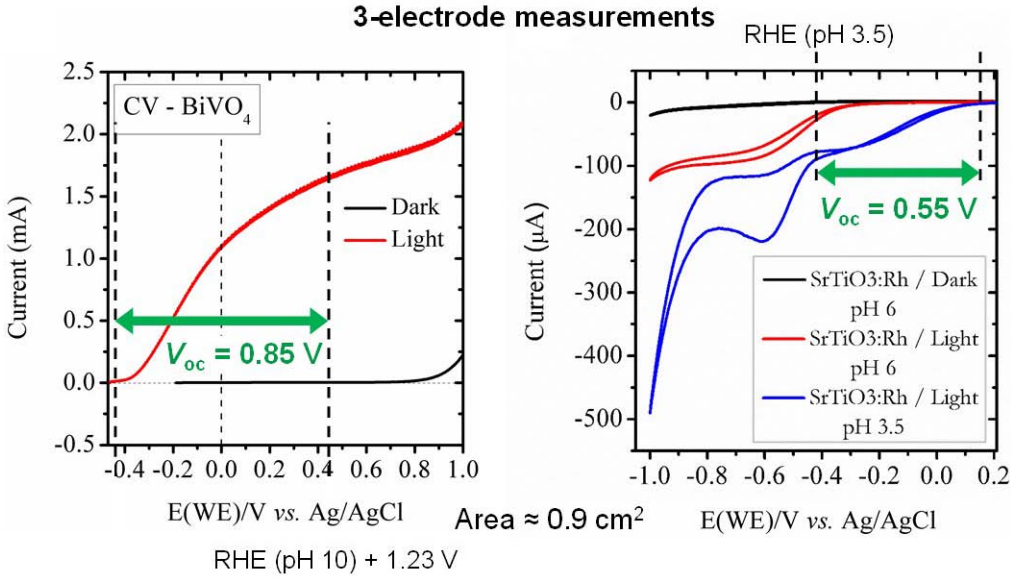


FIGURE 4. Open-circuit photovoltage over time for one-to-few TiO_2 nanoparticles covalently attached to a single nanopore in a poly(ethylene terephthalate) thin film when wetted on both sides by aqueous electrolyte that did or did not contain methanol. Illumination times are indicated by the hashed or yellow highlights.



RHE – Reversible hydrogen electrode

FIGURE 3. Three-electrode current–potential behavior for photoelectrodes immersed in aqueous electrolyte, illuminated with simulated 1 Sun irradiance, and consisting of particles of (a) $BiVO_4$ and (b) Rh-modified $SrTiO_3$

poly(ethylene terephthalate) containing covalently-linked TiO_2 nanoparticle(s). This response is due to electrostatic charging of the interface and is interesting because for the first time, a photovoltage response was measured from one-to-several nanoparticles completely wetted by electrolyte. These results are important to achieving DOE targets because they demonstrate that the photoelectrochemical properties of one-to-few nanoparticle(s) can be measured under relevant conditions.

CONCLUSIONS AND FUTURE DIRECTIONS

Numerical models and simulations suggest that a dual bed reactor consisting of stacked compartments and no convection can achieve at least a 1% STH efficiency. Next, we will assess this concept experimentally using benchtop-scale prototypes, and we expect that a ~12-inch by ~12-inch model reactor of this design will be capable of generating >3 L of H_2 per 8 hours of solar illumination.

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