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
• New end date: June 30, 2018
  (35-month period of performance)

Project Budget

• Total budget: $1,248,063
  – Federal funds: $ 993,759
  – UCI cost share: $ 254,304

• Funding by year (UCI only)
  – Years 1 – 2 spent: $ 571,658
  – Years 1 – 2 budget: $ 726,324
  – Year 3 spent*: $ 109,595
  – Year 3 budget: $ 0

* as of 3/31/2018

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

Particle-slurry Design (this work)
- 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
DOE Barriers

(AJ) Synthesis and Manufacturing

(AG) Integrated Device Configurations

(AH) Reactor Designs

(AI) Auxiliary Materials

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

August 2016 Objective: **Numerically demonstrate** that the *new reactor design* can sustain a ≥ 1% solar-to-hydrogen (STH) conversion efficiency

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>2011</th>
<th>2015</th>
<th>Proposed</th>
<th>2020</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Cost ($/kg)</td>
<td>N/A</td>
<td>28.60</td>
<td>20.00</td>
<td>4.60</td>
<td>2.10</td>
</tr>
<tr>
<td>η&lt;sub&gt;STH&lt;/sub&gt; (%)</td>
<td>N/A</td>
<td>1.0</td>
<td>1.0</td>
<td>5.0</td>
<td>10</td>
</tr>
</tbody>
</table>

*The most important and impactful advances over the past year are underlined*
Approach: General Concept

Current "Type 2"

Cost Sensitivity ($ per kg H$_2$)

- Base Case: 5.0%, 1x, 5 years
- Efficiency: 7.5/5.0/2.5 %
- Particle Cost Multiplier: 0.1/1/20x
- Lifetime: 10/5/1 years

$4.39 at 5% to 5%

Type 2

New Stacked-Reactor Design

("Type 2b")

Cost Sensitivity ($ per kg H$_2$)

- Base Case: 5.0%, 1x, 5 years
- Efficiency: 7.5/5.0/2.5 %
- Particle Cost Multiplier: 0.1/1/20x
- Lifetime: 10/5/1 years

$2.87 at 5%

- Serial light absorption increases efficiency
- Much smaller mass transport distances

Approach: Overview of RD&D

- **Photoelectrochemistry and lab-scale reactors**
- **Iterative computational and experimental approach**
- **Device physics modeling and simulations**

Diagram showing a large-scale reactor with H₂ collection, O₂, and a porous separator. Also, a lab-scale prototype, electrode or small cell, and single-to-few particles.
Approach: R&D Materials Choices

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

<table>
<thead>
<tr>
<th>HER light absorber</th>
<th>HER cocatalyst (wt%)</th>
<th>OER light absorber</th>
<th>OER cocatalyst (concentration (mM), pH)</th>
<th>Aqueous electrolyte (concentration (mM), pH)</th>
<th>Activity measurement</th>
<th>Quantum yield, % (wavelength (nm))</th>
<th>Year\textsuperscript{ref}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaON</td>
<td>Pt (0.3)</td>
<td>WO\textsubscript{3}</td>
<td>Pt (0.5)</td>
<td>NaI (5, 7)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>24</td>
<td>0.4 (420)</td>
</tr>
<tr>
<td>CaTaO\textsubscript{2}N</td>
<td>Pt (0.3)</td>
<td>WO\textsubscript{3}</td>
<td>Pt (0.5)</td>
<td>NaI (5)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>~5.5</td>
<td>n.r.</td>
</tr>
<tr>
<td>BaTaO\textsubscript{2}N</td>
<td>Pt (0.3)</td>
<td>WO\textsubscript{4}</td>
<td>Pt (0.5)</td>
<td>NaI (5)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>~6.5</td>
<td>~3.0</td>
</tr>
<tr>
<td>TaON</td>
<td>Pt (0.3)</td>
<td>TaON</td>
<td>RuO\textsubscript{2} (0.3)</td>
<td>NaI (1, 6)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>~10</td>
<td>~4</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}-TaON</td>
<td>Pt (1, 0.5)</td>
<td>WO\textsubscript{3}</td>
<td>Pt (0.5)</td>
<td>NaI (1, 0, 0.5)\textsuperscript{d}</td>
<td>Xe (n.r., 420–800)\textsuperscript{c}</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}-TaON</td>
<td>Pt (1)</td>
<td>TiO\textsubscript{2}-Ta\textsubscript{2}N\textsubscript{5}</td>
<td>Ir (5)</td>
<td>NaI (0.1)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>~7</td>
<td>~1</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Cr,Ta</td>
<td>Pt (0.5)</td>
<td>WO\textsubscript{3}</td>
<td>PtO\textsubscript{2} (0.5)</td>
<td>NaI (10, 4)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>32</td>
<td>16</td>
</tr>
<tr>
<td>Coumarin-H\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17}</td>
<td>Pt (0.5)</td>
<td>WO\textsubscript{3}</td>
<td>IrO\textsubscript{2} (0.5) and KI (5)</td>
<td>NaI (10, 4)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>2.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Carbazole-H\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17}</td>
<td>Pt (0.5)</td>
<td>WO\textsubscript{3}</td>
<td>IrO\textsubscript{2} (0.5) and KI (5)</td>
<td>NaI (10, 4)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>1.7</td>
<td>0.7</td>
</tr>
<tr>
<td>BaTiO\textsubscript{3}-Rh</td>
<td>Pt (0.25)</td>
<td>WO\textsubscript{3}</td>
<td>PtO\textsubscript{2} (0.5 (Pt))</td>
<td>NaI (10)</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>1.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>HER light absorber</th>
<th>HER cocatalyst (wt%)</th>
<th>OER light absorber</th>
<th>OER cocatalyst (concentration (mM), pH)</th>
<th>Aqueous electrolyte (concentration (mM), pH)</th>
<th>Activity measurement</th>
<th>Quantum yield, % (wavelength (nm))</th>
<th>Year\textsuperscript{ref}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Pt (0.5)</td>
<td>Bi\textsubscript{2}Mo\textsubscript{6}O\textsubscript{8}</td>
<td>None</td>
<td>FeCl\textsubscript{3} (2, 2.4 w/ H\textsubscript{2}SO\textsubscript{4})</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>~20</td>
<td>~10</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Pt (0.5)</td>
<td>WO\textsubscript{3}</td>
<td>None</td>
<td>FeCl\textsubscript{3} (2, 2.4 w/ H\textsubscript{2}SO\textsubscript{4})</td>
<td>Xe (n.r., &gt;420)\textsuperscript{f}</td>
<td>~24</td>
<td>~11</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Ru (0.7)</td>
<td>Bi\textsubscript{4}O\textsubscript{4}</td>
<td>None</td>
<td>FeCl\textsubscript{3} (2, 2.4 w/ H\textsubscript{2}SO\textsubscript{4})</td>
<td>Xe (100, &gt;420)\textsuperscript{f}</td>
<td>130</td>
<td>64</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Ru (0.7)</td>
<td>TiO\textsubscript{2}-Cr,Sb</td>
<td>None</td>
<td>[Co(phen)]\textsubscript{3}Cl\textsubscript{2} (1, 7)</td>
<td>Xe (100, &gt;420)\textsuperscript{f}</td>
<td>7.9</td>
<td>3.5</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Ru (0.7)</td>
<td>Bi\textsubscript{4}O\textsubscript{4}</td>
<td>None</td>
<td>[Co(phen)]\textsubscript{3}SO\textsubscript{4} (1, 7)</td>
<td>Xe (100, &gt;420)\textsuperscript{f}</td>
<td>3.0</td>
<td>0.8</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Ru (0.7)</td>
<td>Bi\textsubscript{4}O\textsubscript{4}</td>
<td>None</td>
<td>[Co(bpy)]\textsubscript{3}SO\textsubscript{4} (0.5, 3.8)</td>
<td>Xe (100, &gt;420)\textsuperscript{f}</td>
<td>100</td>
<td>47</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-Rh</td>
<td>Ru (0.5)</td>
<td>PSII</td>
<td>None</td>
<td>Fe(CN)\textsubscript{6}^{3−/4−} (5, 6)</td>
<td>Xe (250, &gt;420)\textsuperscript{f}</td>
<td>~80\textsuperscript{d}</td>
<td>~40\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Energy Environ. Sci., 2015, 8, 2825
# Approach: Milestones

<table>
<thead>
<tr>
<th>Description of Milestone</th>
<th>Due Date (Quarter)</th>
<th>Percentage Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 1.0</strong> Numerical modeling and simulations of new reactor design</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D1.1.1 Go/No-Go Decision:</strong> Using 80% less pipes and 80% less pumping energy, verify 1% $\eta_{STH}$. (AH, AI) – in silico, demonstrated sustainable reactors that require no pumps or pipes; reaction conditions could be sustained when operating at a 10% $\eta_{STH}$ or smaller (See Technical Backup Slides)</td>
<td>August 1, 2016 (Q4)</td>
<td>100%</td>
</tr>
<tr>
<td><strong>M1.1.3</strong> To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow. (AH, AI) – each of these processes, plus determination of $\eta_{STH}$ limits, has been implemented, at least in part</td>
<td>July 1, 2018 (&quot;Q12&quot; / end)</td>
<td>90%</td>
</tr>
</tbody>
</table>
Accomplishments: Maximum STH Efficiency

Specific tandem baggie reactors ($E_{\text{shuttle}} = 0.36 \text{ V or } 1.06 \text{ V vs RHE}$) have the same maximum STH efficiency as a solid-state tandem.
Accomplishments: Maximum STH Efficiency

The maximum possible STH efficiency for any rapid and perfectly selective redox shuttle is > 60% of the global maximum STH efficiency, which is the maximum efficiency for a solid-state tandem.

Maximum STH efficiency limited by light in the top reactor as follows:
1) Absorption by top OER particles
2) Transmission to bottom HER particles
3) Transmission to bottom OER particles
4) Absorption by top HER particles

Sam Keene
Physicist
(UCI Ph.D. Student)
Accomplishments: Back reactions

Asymmetric redox shuttle electrocatalysis disfavors shunting reactions and will allow for efficient photocatalyst particles

Butler-Volmer equation

\[
\dot{j} = \dot{j}_{0,\text{sh}} \left( \frac{\alpha_{\text{c,sh}} F \eta}{RT} - e^{-\frac{\alpha_{\text{c,sh}} F \eta}{RT}} \right)
\]

\text{prediction is that activity will be > 80% of that simulated to occur in the absence of back reactions}

Other Modeling and Simulation Results (not described in detail on slides elsewhere)

- Transport is more rapid with natural convection due to temperature gradients
- Models supported by experiments conducted on mixing due to temperature gradients
- Mie theory for photocatalyst optical effects (Maxwell’s equations) is more accurate
- A single-photocatalyst-nanoparticle kinetic model is more accurate than bulk equations

Rohini Bala Chandran
Mechanical Engineer
(LBNL Postdoc; Asst. Prof. at U. Mich.)
<table>
<thead>
<tr>
<th>Description of Milestone</th>
<th>Due Date (Quarter)</th>
<th>Percentage Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 1.0 Numerical modeling and simulations of new reactor design</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D1.1.1 Go/No-Go Decision:</strong> Using 80% less pipes and 80% less pumping energy, verify 1% $\eta_{\text{STH}}$. <em>(AH, AI)</em> – in silico, demonstrated sustainable reactors that require no pumps or pipes; reaction conditions could be sustained when operating at a 10% $\eta_{\text{STH}}$ or smaller <em>(See Technical Backup Slides)</em></td>
<td>August 1, 2016 <em>(Q4)</em></td>
<td>100%</td>
</tr>
<tr>
<td><strong>M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow. <em>(AH, AI)</em> – each of these processes, plus determination of $\eta_{\text{STH}}$ limits, has been implemented, at least in part</strong></td>
<td>July 1, 2018 <em>(&quot;Q12&quot; / end)</em></td>
<td>90%</td>
</tr>
<tr>
<td><strong>Task 2.0 Experimental evaluation of chemicals, materials, and reactors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>M2.3.2 Demonstrate &gt; 1% $\eta_{\text{STH}}$ in electrode form factor. <em>(AJ, AG)</em> – 0.1% $\eta_{\text{STH}}$ demonstrated using Rh:SrTiO$_3$ and BiVO$_4$, which was limited by the HER photoelectrode; alternative HER particles, syntheses, and dopants are being explored, with limited success</strong></td>
<td>May 1, 2017 <em>(Q7)</em></td>
<td>30%</td>
</tr>
<tr>
<td><strong>M2.4.1 Demonstrate &gt; 3 L H$_2$ (and &gt; 1.5 L O$_2$) from 8 hours of solar illumination. <em>(AJ, AG, AH, AI)</em> – built and tested model reactors with 10x smaller illumination area than final deliverable; detected H$_2$ by mass spectrometry during visible-light excitation of a smaller reaction vessel; obtained apparent quantum yields that are consistent with state-of-the-art literature reports</strong></td>
<td>July 1, 2018 <em>(&quot;Q12&quot; / end)</em></td>
<td>40%</td>
</tr>
</tbody>
</table>
Accomplishments: Rh:SrTiO₃ Photocatalysts

H₂ measured from illuminated photocatalysts in 1 cm "tall" reactor containing aqueous Fe(II) redox shuttle

thermodynamically, electrons reduce Fe(III) over H⁺

Size of symbol proportional to [Fe(II)]

Relative Quantum Yield for H₂

Argon Tank
Mass Spec
Membrane
Vent
Septum
Particle 1
Particle 2

Sam Keene
Physicist
(UCI Ph.D. Student)
Addition of Ru cocatalysts increases quantum yield for H₂ with decreased dependence on [Fe(III)]; hydroquinone is also a good donor.

**Other Experimental Results (not described in detail on slides elsewhere)**
- Doped and co-doped SrTiO₃ materials were synthesized by various routes
- Low activity for the HER using PEDOT:PSS/La₅Ti₂CuS₅O₇ photoelectrodes
- Some electrochemical selectivity by the cocatalysts for the HER/OER
Accomplishments: Quantum Yield Comparisons

**Rh: SrTiO$_3$ HER photocatalysts** (*405 nm excitation*)

<table>
<thead>
<tr>
<th>Redox species</th>
<th>no cocatalysts</th>
<th>with Ru cocatalysts</th>
<th>notes (* all with argon flow*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol (<em>sacrificial</em>)</td>
<td>~0%</td>
<td>0.6%</td>
<td>no pH adjustment</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.3%</td>
<td>1.0%</td>
<td>same response at pH 1 – 2.4; no response at high pH</td>
</tr>
<tr>
<td>hydroquinone</td>
<td>~0%</td>
<td>0.09%</td>
<td>no pH adjustment; reducing pH had no effect</td>
</tr>
<tr>
<td>iodide</td>
<td>0%</td>
<td>0%</td>
<td>pH 7 and 11 investigated</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conditions</th>
<th>cococatalyst type</th>
<th>rate of H$_2$ Production (μmol h$^{-1}$)</th>
<th>quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduced pressure</td>
<td>Pt</td>
<td>1.3, with methanol (<em>sacrificial</em>)</td>
<td>0.7%</td>
</tr>
<tr>
<td>nitrogen flow</td>
<td>Pt</td>
<td>3.7, with methanol (<em>sacrificial</em>)</td>
<td>2.1%</td>
</tr>
<tr>
<td>argon flow</td>
<td>Pt</td>
<td>4.4, with methanol (<em>sacrificial</em>)</td>
<td>2.4%</td>
</tr>
<tr>
<td>reduced pressure</td>
<td>Ru</td>
<td>2.0, with methanol (<em>sacrificial</em>)</td>
<td>1.1%</td>
</tr>
</tbody>
</table>

**Mo: BiVO$_4$ OER photocatalysts** (*405 nm excitation*)

<table>
<thead>
<tr>
<th>Redox species</th>
<th>without cocatalysts</th>
<th>notes (* all with argon flow*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(I) (<em>sacrificial</em>)</td>
<td>2.6%</td>
<td>no pH adjustment</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>1.5%</td>
<td>pH 2</td>
</tr>
<tr>
<td>quinone</td>
<td>0</td>
<td>no pH adjustment</td>
</tr>
<tr>
<td>IO$_3^-$</td>
<td>0</td>
<td>pH 7 and 11 investigated</td>
</tr>
</tbody>
</table>

Similar Q.Y. for OER (Mo:BiVO$_4$) and HER (Rh: SrTiO$_3$)
Response to previous year reviewers’ comments

“When measured toward Hydrogen and Fuel Cells Program goals, the project is an order of magnitude away, and it is difficult to see a pathway for it to achieve overall goals.” / “The project might drop the three-liter demonstration if it is a large distraction.”

This project aimed to realize an increase in the STH efficiency of photocatalyst reactors using several new approaches. These approaches were not very successful and were further hampered by poor materials performance. Therefore, the focus in the final months of the project has shifted away from the 3 SLH₂ demonstration, and instead on understanding photocatalyst reactivity and disseminating this to the community. This project was funded under an Incubator FOA and so it was intended to be slightly higher risk.

“The researchers want to achieve a cost target of $20/kg H₂ while achieving a 1% solar efficiency. Put another way, if they somehow miraculously achieved 20% efficiency, their costs would be $1/kg H₂.” / “Regarding modeling, the project might consider generating theoretical STH iso-contour plots with E_g₁ and E_g₂ on the x- and y-axes”.

A techno-economic analysis using the H₂A tool was conducted and it suggests that this new design is cost-effective. (The efficiency and cost do not scale linearly.) Results from our STH efficiency models were unexpected and will help guide future research.

“It is clearly time to put real particle suspensions in the baggie and see what happens. It would be best if they can find time to develop a model of the nanoparticles before they start fabricating them.” / “What is really needed is better [PEC] materials”.

For nearly one year, we have been measuring the STH efficiency from particle suspensions. The quantum yields are as expected based on the literature. A device physics model is currently under development for single particle photochemistry, but it is still incomplete.
Collaborations

Primary team members *(funded)*

- Lawrence Berkeley National Laboratory (Federal Lab) & Joint Center for Artificial Photosynthesis (DOE Hub)
  - **Adam Weber (sub-recipient; part of HydroGEN):** Core numerical device-multi-physics modeling and simulation effort with unique expertise in coupled transport phenomena
- California Institute of Technology (University) & Joint Center for Artificial Photosynthesis (DOE Hub)
  - **Chengxiang Xiang (sub-contracted advisor; part of HydroGEN):** Unique expertise in numerical device-multi-physics modeling and simulation of related photoelectrochemical devices

Additional team members with materials synthesis expertise *(unfunded)*

- Tokyo University of Science, **Akihiko Kudo (Rh: SrTiO\(_3\), BiVO\(_4\))**
Remaining Challenges and Barriers

Task 1.0  Numerical modeling and simulation of new reactor design

• Complete analyses for STH efficiency dependence on bandgap energies and potential of the redox shuttle.
• Complete complex fluid flow model to enable simulation of convection, e.g. pumping/mixing, thermal effects.
• Complete advanced optical phenomena model to more accurately model E&M and particle photophysics.
• Complete more accurate model for photocatalyst reactivity by modeling individual reactions on particles instead of baggie ensemble behavior as an ideal diode coupled to empirical Butler–Volmer electrokinetics.

Task 2.0  Experimental evaluation of chemicals, materials, and reactors

• Complete photocatalyst performance measurements and perform several parametric studies.
• Complete studies on selective electrocatalysis at electrodes for the HER/OER versus redox shuttle reactions.
• Complete analyses of temperature gradient effects on natural convection in prototypes.
• 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% $\eta_{\text{STH}}$ in electrode form factor and as particle suspensions, as prerequisites to the original final deliverable of > 3 SLH$_2$ from 8 hours of solar illumination.

Any proposed future work is subject to change based on funding levels.
# Proposed Future Work

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

<table>
<thead>
<tr>
<th>Description of Milestone – Solution</th>
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<tr>
<td><strong>Task 1.0 Numerical modeling and simulation of new reactor design</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1.1.3 To the model, add electromagnetic wave propagation, thermal effects, and multi-phase flow – <strong>Introduce these phenomena into the master modeling framework and validate results from the simulations; also determine the efficiency limits of these types of reactors as a function of redox shuttle</strong></td>
<td>July 1, 2018 (&quot;Q12&quot; / end)</td>
<td>90%</td>
</tr>
<tr>
<td><strong>Task 2.0 Experimental evaluation of chemicals, materials, and reactors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2.3.2 Demonstrate &gt; 1% $\eta_{\text{STH}}$ in electrode form factor – <strong>Using efficient thin-film and mesoporous electrodes with photochemically deposited electrocatalysts, optimize conditions</strong></td>
<td>May 1, 2017 (Q7)</td>
<td>30%</td>
</tr>
<tr>
<td>M2.4.1 Demonstrate &gt; 3 standard L of H₂ (and &gt; 1.5 L of O₂) from 8 hours of solar illumination – <strong>Using electrodes and free-floating particles, continue to assess the impacts that redox shuttles have on the rate of H₂ evolution; introduce selective catalysis through interfacial engineering of light absorbers and catalysts; combine particles, prototype reactors, and redox shuttles and measure rates of H₂ evolution under solar illumination</strong></td>
<td>July 1, 2018 (&quot;Q12&quot; / end)</td>
<td>40%</td>
</tr>
</tbody>
</table>

*Additional funding to support follow-on work has not yet been obtained*

Any proposed future work is subject to change based on funding level.
**Project Summary**

**Project Objective:** Experimentally validate a new design for scalable solar-H$_2$ technologies using laboratory-scale prototype particle suspension reactors

<table>
<thead>
<tr>
<th>Relevance</th>
<th>Techno-economic analyses of particle suspension reactors with side-by-side compartments suggest that H$_2$ cost may be rather inexpensive.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approach</td>
<td>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.</td>
</tr>
<tr>
<td>Technical Accomplishments</td>
<td>Using a validated device physics model, we numerically demonstrated stable operation of a tandem reactor operating at up to a 10% STH efficiency and assuming most relevant physics. We also synthesized and characterized efficient photoelectrodes consisting of Rh-modified SrTiO$_3$, WO$_3$, or BiVO$_4$ and for each of these, demonstrated photocurrents at a rate consistent with a 1% STH efficiency. We also developed prototype reactors and techniques to locally assess redox shuttle concentration <em>in situ</em>. <strong>We also demonstrated state-of-the-art quantum yields from our materials as nanoparticle suspensions.</strong></td>
</tr>
<tr>
<td>Collaborations</td>
<td>Weber / Xiang for numerical modeling; Kudo for materials synthesis.</td>
</tr>
<tr>
<td>Proposed Future Work</td>
<td>Add additional device physics to the numerical models and synthesize high quality metal-oxide particles that attain a large quantum yield.</td>
</tr>
</tbody>
</table>
Technical Backup Slides
Half of this cost is due to PVC pipes & pumps

Prior Accomplishments: 10% STH Model

Steady-periodic conditions for **10% STH efficiency**
with zero convection (indefinite operation)

- Beer’s Law for optimal light absorber photodiodes
- State-of-the-art electrocatalysis & Butler–Volmer parameters
- Light absorption by IO$_3^-$/$I^-$ redox shuttle within solubility limits
- Redox shuttle transport governed by diffusion and drift
- Non-H$^+$ counterion for redox shuttle (adjustable pH)
- Separator thickness and porosity limit H$_2$/O$_2$ crossover
Prior Accomplishments: Lab Prototypes

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

Kevin Tkacz
Materials Scientist
(UCI Ph.D. Student)
**Prior Accomplishments: Separators**

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

A suitable nanoporous separator has not been identified.
Prior Accomplishments: PEC Electrodes

Rh-modified SrTiO₃ and BiVO₄ can generate > 1.23 V, but efficiency is limited by Rh:SrTiO₃ $J \approx 0.1$ mA cm$^{-2}$

Houman Yaghoubi
Electrical Engineer
(UCI Postdoc; Senior Scientist at Genalyte)