BES023 Joint Center for Artificial Photosynthesis: Modeling and Simulation Team

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Objectives

The mission of the Joint Center for Artificial Photosynthesis (JCAP) is to produce fundamental scientific discoveries and major technological breakthroughs to enable the development of energy-efficient, cost-effective, and commercially viable processes for the large-scale conversion of sunlight directly to fuels. JCAP's 5-year goal is discovery of robust, Earth-abundant light absorbers, catalysts, linkers, membranes, and scale-up science required to assemble the components into a complete artificial photosynthetic system. The Modeling and Simulation Team (MaST) develops state of the art multi-scale, multiphysics continuum models of the various processes occurring within the integrated photoelectrode cells.

Technical Barriers

To identify materials that can operate in a solar fuels device, material screening must be performed under technologically-relevant conditions. High throughput instruments that adhere to these conditions must be developed and then automated to provide robust high throughput operation. This screening strategy must then be imbedded in a high throughput pipeline that includes high quality materials synthesis and characterization. While operation of this pipeline can identify new promising materials, accelerated discovery, development and deployment of materials can only be attained by integrating the high throughput pipeline in a larger effort that includes benchmarking, directed research and prototyping efforts. Successful implementation of this research paradigm also requires interplay with theory efforts. JCAP is boldly solving these exciting technical and research integration challenges.

Abstract

Modeling and simulation at the continuum level has been used for years to help interpret and guide experimental investigations of electrochemical technologies, in particular, fuel cells and batteries. The same principles can be applied to new areas such as photoelectrochemical cells that produce fuels from sunlight. It is the objective of the Modeling and Simulation Team (MaST) at JCAP to provide such knowledge in this area. MaST provides guidance, examined tradeoff analysis between material and physical properties, helps to set design targets to the JCAP projects, guides experiments for model input and validation, provides scale-up and prototype guidance, and interacts with the external community with respect to modeling photoelectrochemical-cell phenomena. Specific issues to be discussed in this poster include examination of the design space for solar-fuel generators including alternate designs; the impact of operation at near-neutral pH, and optimization of component design targets.

Progress Report

Operation of PEC at near-neutral pH

There is a desire to operate PECs at neutral or near-neutral pH conditions in order to mitigate corrosion and enable easier fluid handling. This has been shown to be accomplished in single, stirred reactors through the use of buffers and supporting electrolyte so as not to increase ohmic losses in the system. However, there is also a need to minimize product crossover and thus generate pure hydrogen. Such separation necessitates the use of some kind of separator, typically an ion-exchange membrane like Nafion. Modeling and simulation is an ideal tool to explore the operation of such PECs and identify the feasibility of operation at near-neutral pH.

The overpotentials during operation can be seen as being due to the reaction overpotentials at the anode (oxygen evolution), cathode (hydrogen evolution), transport by diffusion, ohmic losses, and transport due to the protons (pH), which are reactive species at the electrodes. For a low-pH system (i.e., sulfuric acid) using state-of-the-art material properties and Nafion as a separator, continuum simulations can be used to show the breakdown of the overpotentials as shown in Figure 1a. From the figure, it is clear that one can theoretically operate at very high current densities (of course real operation in a PEC depends on how the load curve intersects with the PV power curve, which is ignored in this study). For comparison, Figure 1b shows

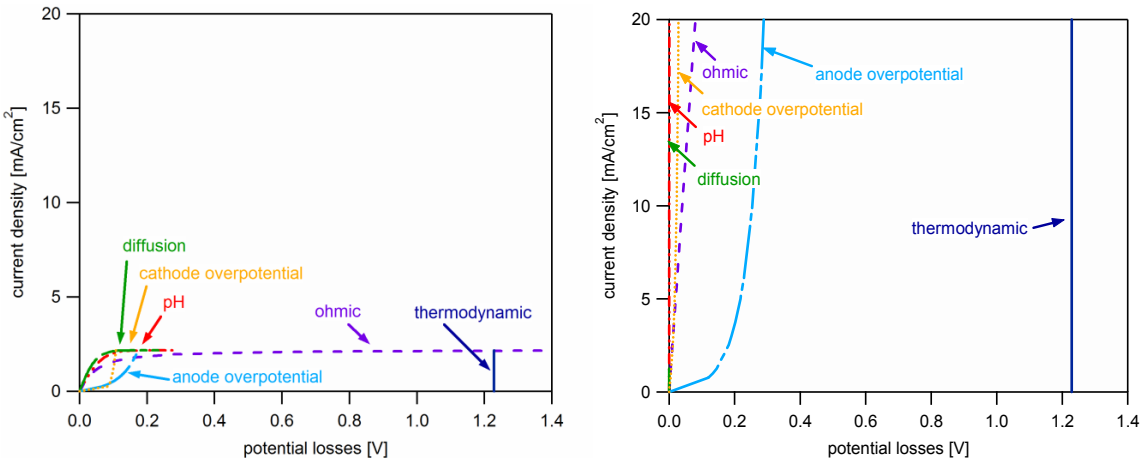

FIGURE 1. Overpotential losses at (a) pH = 0 for sulfuric acid and (b) pH = 9.2 for a borate buffer.

the same overpotential breakdown for the case of a borate buffer that operates around pH 9.2. As shown in the figure, the cell can no longer obtain higher current densities due to the very large ohmic potential that develops at steady state. The genesis of this overpotential can be understood in that during operation, electrodialysis of the solution occurs. Thus, the generation(consumption) of protons at the anode(cathode) results in more neutral acid in the anode and similarly more anions in the cathode, which drives the positive salt ions from the anode to the cathode. This cycle effectively decreases the number of charge carriers at the anode and thus results in larger ohmic losses. Similar electrodialysis effects will happen if one tries to use weak acids or supporting electrolyte, where the pH and diffusion losses can become limiting. The results of such simulations are shown in Figure 2, where one can see that operation at even moderate acid conditions results in small obtainable steady-state current densities. Finally, as shown in Figure 3, even if operating with a porous separator and the borate buffer, the pH at the electrodes will still be highly basic due to the migration and diffusion fluxes and the generation/consumption of hydroxide radicals.

PEC designs

Practical PECs are only now beginning to be fabricated and designed. Modeling and simulation can help greatly in examining tradeoffs of kinetics and ohmic losses, current efficiencies and crossover, and hence optimizing designs for various material properties. Such an example is shown in Figure 4, where a back-to-back louvered design is constructed virtually and the current lines and potential drops calculated. One can then use the model to examine

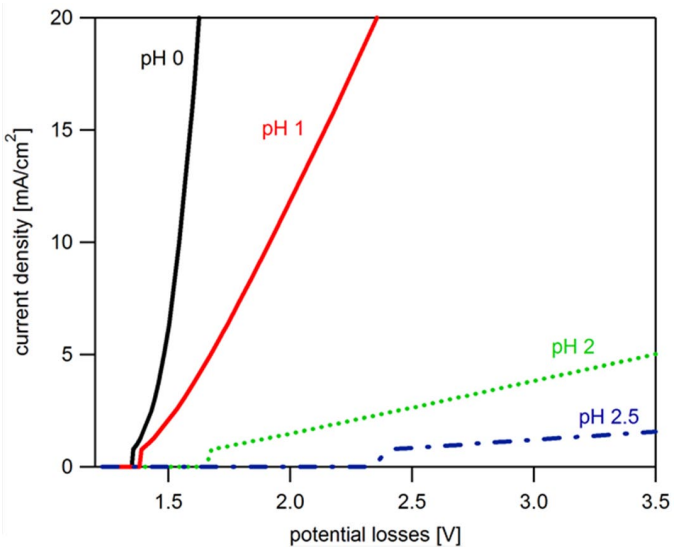

FIGURE 2. Current density as a function of potential losses at different operation pH

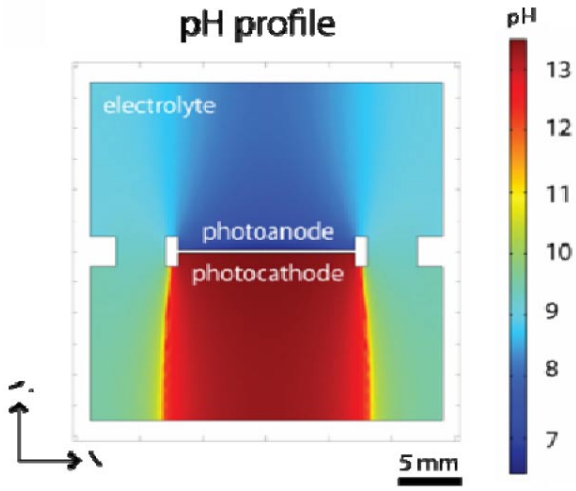

FIGURE 3. pH profile of operating PEC with borate buffer (pH = 9.2)

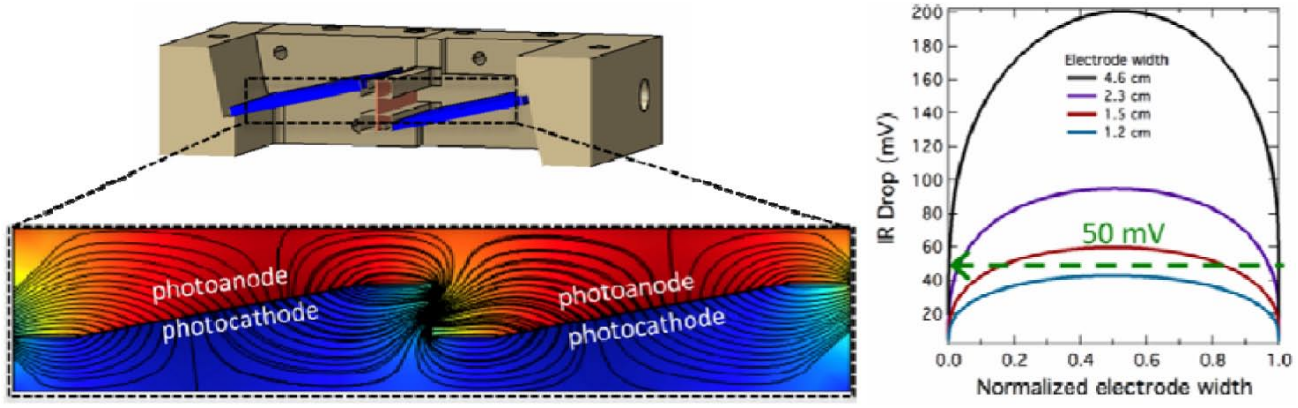

FIGURE 4. Simulated current and potential profiles for a louvered design and examination of the impact of electrode width of such a design on its ohmic losses.

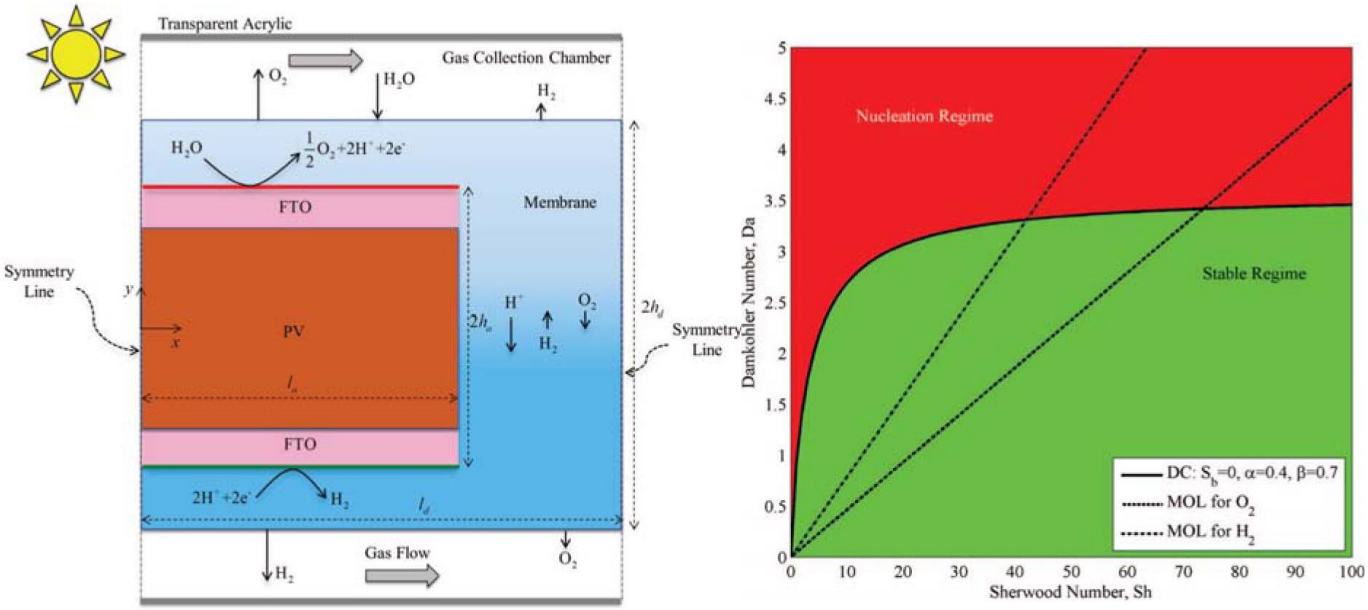

FIGURE 5. (left) Schematic of operation of a PEC with water vapor where the PV and catalyst assembly is embedded in an ion-conducting membrane. (right) Unstable and stable regimes based on material properties and operating conditions of Nafion specific to hydrogen and oxygen transport.

how the ohmic losses change with cell width as shown in the right-side of Figure 4. Here, it is clearly seen that larger electrode widths result in more nonuniform current densities and higher ohmic drops due to the longer proton path-length. In a similar manner, optimized cell dimensions for height, separator thickness, etc. can be derived.

In addition to analyzing current designs, the model has also been utilized to look at newer designs. As shown in Figure 5, one can envision operating on only water vapor instead of liquid water. This can occur because the necessary amount of water for operation at 10 mA/cm^2 (10% efficient conversion of the solar irradiance) is only 3.4 mg/cm^2/hr, which can be supplied by mist or wicks. Operation with vapor can also help to avoid pumping, corrosion, and bubble issues with liquid electrolyte. By simulating the transport of heat, water, protons, and gases through the membrane, one can determine the necessary design space for stable operation as shown in the right-side figure in Figure 5. In such a design, one is worried about supplying enough water for adequate reaction and conductivity, while also minimizing membrane thickness to avoid gas bubbles and delamination.

Examination of optimal band-gap combinations

As mentioned above, operation of a PEC occurs at the intersection of the PV power curve with the load curve as shown in Figure 6. Modeling this intersection and the

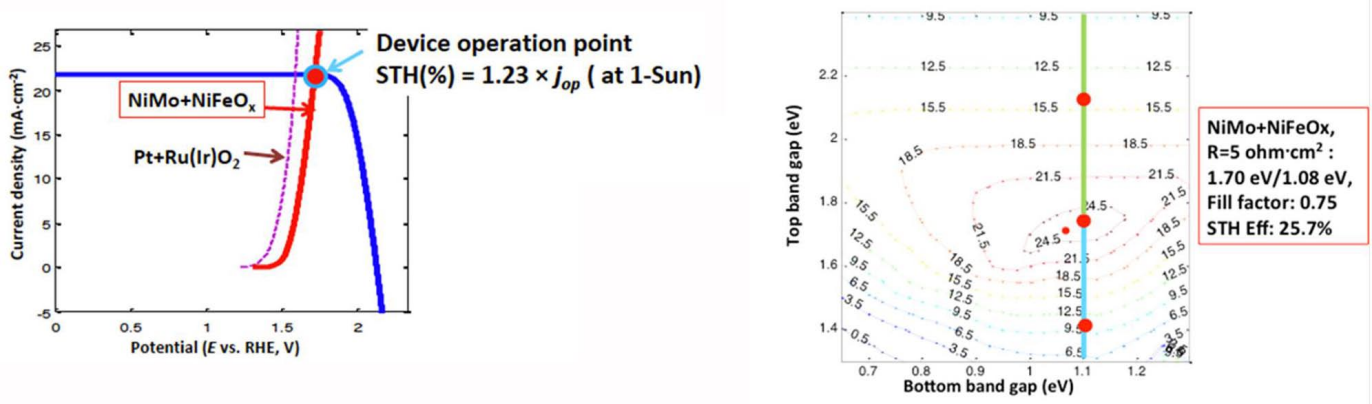

FIGURE 6. PEC operation and model results showing the current density for different bandgap combinations.

associated semiconductor physics along with the ion transport phenomena allows one to optimize and examine the impact of different material properties. Similar to the analysis above for water-vapor PEC, where one could examine the impact of different membrane properties, one can also examine the impact of the semiconductor properties. For example, as shown in Figure 6, for a tandem structure, the choice of the top and bottom bandgaps can be analyzed to set design targets for the material-development efforts within JCAP.

Future Directions

There are several issues that are planned to be addressed in the upcoming year by MaST, including:

- Complete multi-physics model incorporating light capture and semiconductor physics using cross-platform models and software
- Release of the JCAP Modeler to the external community to allow them usage of this resource
- Continued examination of new designs (e.g., concentrator) and phenomena (e.g., bubble existence)
- Sensitivity analysis of key parameters/properties

Selected publication list

1. Haussener, S., Hu, S., Xiang, C., Weber, A.Z., Lewis, N.S., 'Simulations of the Irradiation and Temperature Dependence of the Efficiency of Tandem Photoelectrochemical Water-Splitting Systems', *Energy and Environmental Science* **2013**, *6* (12), 3605-3618.

2. Haussener, S., Xiang, C., Spurgeon, J., Ardo, S., Lewis, N.S., Weber, A.Z., 'Modeling, Simulation, and Design Criteria for Photoelectrochemical Water-Splitting Systems,' *Energy and Environmental Science* **2012**, *5* (12), 9922-9935.

3. Hu, S., Xiang, C., Haussener, S., Berger, A.D., Lewis, N.S., 'An analysis of the optimal band gaps of light absorbers in integrated tandem photoelectrochemical water-splitting systems,' *Energy Environ. Sci.* **2013**, *6*, 2984-2993

4. Berger, A.D., Seglaman, R.A., Newman, J., 'Material Requirements for Membrane Separators in a Water-Splitting Photoelectrochemical Cell,' *Energy Environ. Sci.* **2014.**

5. Singh, M.R., Stevens, J.C, Weber, A.Z., 'Design of Membrane-Encapsulated Wireless Photoelectrochemical Cells for Hydrogen Production,' *J. Electrochem. Soc.* **2014**, in press.

6. Berger, A.D., Newman, J., 'An Integrated 1-Dimensional Model of a Photoelectrochemical Cell for Water Splitting', *J. Electrochem. Soc.* **2014**, in press.

7. Fountaine, K.T., Whitney, W.S., Atwater, H.A. 'Achieving near-unity broadband absorption in sparse arrays of GaAs nanowires via a fundamental understanding of localized radial modes', *Optics Express* **2014**.

8. Shaner, M.R., Fountaine, K.T., Lewerenz, H.J., 'Current-voltage characteristics of coupled photodiode-electrocatalyst devices', *Appl. Phys. Lett*. **2013**, *103*, 143905.

9. Xiang, C., Chen, Y., Lewis, N.S., 'Modeling an integrated photoelectrolysis system sustained by water vapor,' *Energy and Environmental Science* **2013**, *6* (12), 3713-3721.