Two designs for an integrated photoelectrolysis system that uses a 10× concentrating solar collector have been investigated in detail. The system performance was evaluated using a multi-physics model that accounted for the properties of the tandem photocathodes, mass transport, and the electrocatalytic performance of the oxygen-evolution and hydrogen-evolution reactions (OER and HER, respectively). The solar-to-hydrogen (STH) conversion efficiencies and the ohmic losses associated with proton transport in the solution electrolyte and through the membrane of the photoelectrolysis system were evaluated systematically as a function of the cell dimensions, the operating temperatures, the bandgap combinations of the tandem cell, and the performance of both the photocathodes and electrocatalysts. Relative to designs of optimized systems that would operate without a solar concentrator, the optimized 10× solar concentrator designs possessed larger ohmic losses and exhibited less uniformity in the distribution of the current density along the width of the photoelectrode. To minimize resistive losses while maximizing the solar-to-hydrogen conversion efficiency, η_{STH}, both of the designs, a two-dimensional “trough” design and a three-dimensional “bubble wrap” design, required that the electrode width or diameter, respectively, was no larger than a few millimeters. As the size of the electrodes increased beyond this limiting dimension, the η_{STH} became more sensitive to the performance of the photocathodes and catalysts. At a fixed electrode dimension, increases in the operating temperature reduced the efficiency of cells with smaller electrodes, due to degradation in the performance of the photocathode with increasing temperature. In contrast, cells with larger electrode dimensions showed increases in efficiency as the temperature increased, due to increases in the rates of electrocatalysis and due to enhanced mass transport. The simulations indicated that cells that contained 10% photocathode area, and minimal amounts of Nafion or other permselective membranes (i.e. areal coverages and volumetric fractions of only a few percent of the cell), with the remaining area comprised of a suitable, low-cost inert, non porous material (flexible polymers, inert inorganic materials, etc.) should be able to produce high values of η_{STH}, with η_{STH} = 29.8% for an optimized design with a bandgap combination of 1.6 eV/0.9 eV in a tandem photoelectrolysis system at 350 K.

© The Author(s) 2014. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.075140jes] All rights reserved.

Artificial photosynthesis could provide a promising route to large-scale solar energy conversion and storage. Recent techno-economic studies have evaluated various designs for integrated photoelectrolysis systems, including a very promising system that makes use of concentrated illumination. A discrete III-V photovoltaic cell connected electrically in series with a discrete polymer-electrolyte membrane (PEM) electrolyzer has demonstrated a solar-to-hydrogen (STH) conversion efficiency of 18% under 500 Suns. Although concentrated photovoltaics (CPV) typically incorporate multi-stage optical systems to achieve high optical concentration (~ 400 Suns to 1200 Suns), integrated photoelectrochemical systems for large scale, distributed solar-to-fuel applications are most likely operate efficiently and scalably at lower solar concentration factors (5 – 100) due to limitations associated with electrocatalytic overpotential losses, ohmic losses, and mass transport restrictions associated with high current densities in a system operating under very concentrated sunlight. Notably, systems that utilize a low-multiple concentrating solar collector, such as a 10× concentrator, requires little or no active solar tracking or temperature-regulation systems. Conceptual designs of coupling low concentrator solar collectors with a photoelectrochemical cell have been proposed. A principal advantage of a sunlight-concentrating design for a solar-to-fuels generator is the potential reduction of the usage per unit area of photocathode materials, which could result in a significant reduction in the system cost. Although extensive modeling and simulation efforts have been completed for solar fuel generator system designs without solar concentrators, including various operating conditions and using different types of input feed-stocks including liquid electrolytes and water vapor feeds, the design criteria and constraints for an integrated system that exploits concentrating solar collectors have not yet been evaluated.

The high-intensity illumination, and the expected elevated operating temperatures in a light-concentrating photoelectrolysis system, could have significant impacts on the performance of the individual components of the system, and thus on the efficiency of the system as a whole. Increases in the illumination intensity would increase the photocurrent density and would concomitantly improve the open-circuit voltage and the fill factor of the current-voltage characteristic of the photovoltaic materials. The increased current density would also, however, result in an increase in the ohmic losses of the cell, as well as produce an increase to the overpotentials required to drive the oxygen-evolution reaction (OER) and the hydrogen-evolution reaction (HER). Increases in the operating temperatures would introduce similar trade-offs to the design system, because the increased temperature would degrade the performance of the semiconducting light absorbers while improving both the mass transport in the electrolyte and the performance of the HER and OER catalysts. As a result, the overall system efficiency as a function of the cell geometry, the illumination intensity, and the operating temperature depends upon the working principles for each component as well as upon the detailed mathematical relationships between the components.

Previously reported results from the modeling of integrated photoelectrolysis system designs without solar concentrators have shown that the geometric parameters of the cell dominate the cell performance. Specifically, the width of the photoelectrode must be less than a few centimeters to minimize the ohmic losses from the ionic transport in the electrolyte and membrane. At the higher operating current density produced by concentrated sunlight, the details of the cell geometry are likely to play an even more important role. Although a smaller cell will typically reduce the efficiency losses due to mass transport in the electrolyte, the assembly and integration of absorber materials and other system components could be easier with macroscopic, rather than microscopic, components. Thus, an optimal design would likely maximize the photoelectrode width while minimizing any efficiency losses due to mass transport limitations and ohmic losses.

In this work, two types of integrated photoelectrolysis systems that use a concentrated light source have been investigated: a two-dimensional “trough” design and a three-dimensional “bubble wrap” design. The concentration of the illumination was chosen to be ten-fold relative to natural sunlight. The solar-to-hydrogen (STH) conversion
efficiency for the systems, and the ohmic loss as a function of the cell geometry, operating temperatures, and catalyst performance were evaluated systematically using a fully coupled model for the system as a whole. We have also evaluated the requirements for the size and placement of a proton-exchange membrane, such as Nafion, to minimize the usage of this material, as well as of analogous high-performance polymers, as the permselective gas-blocking component of the system.

Modeling

Cell designs.— Figure 1 presents schematically the two cell designs that were modeled in this work. Both designs include a 10× solar concentrator and an integrated photoelectrolysis assembly. The detailed configuration and construction of the solar concentrator is beyond the scope of this work, but two-dimensional or three-dimensional Fresnel lens, compound parabolic concentrators (CPC), or dielectric totally internally reflecting concentrators could be employed to achieve the 10× solar concentration specified in the designs. For example, with ten-fold concentration, efficient light collection up to 7.5 hours/day can be achieved by compound parabolic concentrators only with occasional tilt adjustments.23 The two-dimensional “trough” design (Fig. 1a) contains a photoelectrode having a width, \( l_e \), with \( l_e \) constrained to be 10% of the total cell width, \( l_c \), consistent with 10× concentrating optics. The photoelectrode was taken to be of infinite length in the out-of-plane direction. The three-dimensional “bubble wrap” design (Fig. 1b) consists of a disk photoelectrode with a diameter, \( d_e \), that was constrained to be 32% of the cell diameter, \( d_c \), again consistent with 10× concentrating optics. Both designs contained Nafion films and insulating plastics to prevent product crossover and for structural support. The Nafion films also provided the required pathways for ionic conduction between the photocathode and photoanode chambers. The detailed construct of the integrated photoelectrochemical cell is shown in Figure 1c. The photoanode and photocathode are each assumed to be coated by a protective transparent conductive oxide (TCO) layer, to maintain uniformity of the current density distribution and minimize the ohmic losses in the system. Oxygen-evolution catalysts were coated on top of the TCO in the photocathode, whereas hydrogen-evolution catalysts were coated on the bottom of the TCO in the photoanode.

Table 1 presents the basic input parameters used in the model. The system performance was evaluated for two pairs of OER and HER catalysts in 1.0 M H2SO4. The “No. 1” catalyst system assumed electrocatalytic properties typical of iridium oxide for the OER and platinum for the HER in acidic conditions, while the “No. 2” catalyst system assumed twice the OER and HER overpotentials exhibited by the “No. 1” catalyst system to produce a current density of 100 mA cm\(^{-2}\) for the anodic and cathodic processes respectively, based on the geometric area of a planar electrode.

Equations describing transport and kinetics.— The ion transport in the electrolyte and in the proton-exchange membrane, as well as the transport of electrons and holes in the TCO coatings, were modeled using Ohm’s law:

\[
j_{el,TCO,mem} = -\sigma_{el,TCO,mem} \nabla \phi_{el,TCO,mem},
\]

where \( \sigma_{el,TCO,mem} \) is the conductivity of the electrolyte, TCO or the membrane (Nafion), respectively, \( \nabla \phi_{el,TCO,mem} \) is corresponding potential drop and \( j_{el,TCO,mem} \) is the corresponding current density.

The kinetics of electrocatalysis at the TCO and at the electrolyte interface for the OER and HER were modeled using the Butler-Volmer equation:

\[
J_{R,OER/HER} = J_{0,OER/HER} \left[ \exp \left( \frac{\alpha_{R,OER/HER} F \eta}{RT} \right) - \exp \left( -\frac{\alpha_{R,OER/HER} F \eta}{RT} \right) \right],
\]

where \( J_{R,OER/HER} \) is the current density for the OER or HER at the electrode/electrolyte interface, \( J_{0,OER/HER} \) is the exchange-current density for the OER or HER, respectively, \( \alpha_{R,OER/HER} \) are the corresponding anodic and cathodic transfer coefficients, respectively, \( F \) is Faraday’s constant, \( R \) is the ideal gas constant, \( T \) is the temperature and \( \eta \) is the overpotential for the reaction, which is defined as

\[
\eta = \phi_i - \phi_e - \phi_0,
\]

where \( \phi_i \) and \( \phi_e \) are the electric and electrolyte potentials at the interface, respectively, and \( \phi_0 \) is the equilibrium potential for the reaction. Conservation of charge and continuity of current density were enforced at both the cathodic and anodic interfaces.

Photocathode and temperature dependence.— The photoelectrode was modeled as two semiconducting light absorbers connected in series. One absorber had a bandgap of 1.7 eV and was located directly on top of the other absorber, which had a bandgap of 1.1 eV. Without solar concentration, such a tandem cell can provide sufficient photovoltage at light-limited current densities to allow the use of earth-abundant catalyst materials in a photoelectrolysis system.18 The STH conversion efficiency as a function of different bandgap combinations with realistic cell geometries was also calculated in this study.
The photovoltage of the tandem photoelectrode at a given operating current density, \( J \), was determined by adding the photovoltages of the serially connected top and bottom half-cells, i.e.:

\[
V_{\text{tandem}}(J) = V_{\text{top}}(J) + V_{\text{bottom}}(J).
\]

The relationship between the current density and voltage of the tandem photoelectrode at a given operating temperature was defined by:

\[
J = J_{\text{ph}} + J_{\text{h}} - J_{\text{rad}}.
\]

The analytical expressions for \( J_{\text{ph}}, J_{\text{h}}, \text{and } J_{\text{rad}} \) are well described in literature.\(^{24,25}\) The operating current density of each half-cell was then calculated numerically at a given photovoltage. 100% of the above-bandgap solar flux was assumed to be absorbed and converted to photocurrent, so the photocurrent density was given by:

\[
J_{\text{ph}} = C \times e \int \frac{E_{g}}{\hbar \omega} \exp \left( \frac{-h \omega}{kT} \right) \, d\omega,
\]

where \( C \) is the concentration factor, \( e \) is the unsigned charge on an electron, \( E_{g} \) is the bandgap of the photoabsorber, \( \Lambda \) is the wavelength-dependent solar flux in the Air Mass (AM)1.5 solar spectrum, \( \hbar \) is an abbreviation for \( h/2\pi \) with \( h \) being Planck’s constant, and \( \omega \) is the frequency of the incident light.

The radiative-emission currents were calculated from the relationship:

\[
J_{\text{rad}} = \frac{e (n_{\text{top}} + n_{\text{bottom}})^2}{4\pi^2c^2} \int_{E_{g}/2}^{\infty} \omega^{2} \exp \left( \frac{-\omega}{kT} \right) d\omega,
\]

where \( n_{\text{top}} \) and \( n_{\text{bottom}} \) are the refractive indexes of the media on the top and at the bottom of the cell, respectively, \( V \) is the operating voltage, \( T \) is the absolute temperature, \( k \) is Boltzmann’s constant, and \( c \) is the speed of light. The thermal radiation currents as a function of \( T \) were given by:

\[
J_{\text{h}} = \frac{e (n_{\text{top}} + n_{\text{bottom}})^2}{4\pi^2c^2} \int_{E_{g}/2}^{\infty} \omega^{2} \exp \left( \frac{-\omega}{kT} \right) d\omega.
\]

The relationship between the current-density and voltage that was obtained from the detailed-balance calculation was then fitted using eq. 9 for an ideal diode coupled with an effective series resistance:

\[
J = J_{\text{ph}} - J_{0} \exp \left[ \frac{e(V + J R_{S})}{kT} \right],
\]

where \( J_{0} \) is saturation current density in the dark, \( V \) is the applied photovoltage, and \( R_{S} \) is the effective series resistance. The fitted value for \( J \) was then used as the boundary condition at the photoelectrode-TCO interface. The effective series resistance was varied to approximate various situations in which the solar cell operated either at the detailed-balance limit or under non-ideal operating conditions in which the fill factor varied from 0.65 to 0.90.

Temperature-dependent conductivity of the electrolyte and membrane.— The conductivity of the electrolyte as a function of the operating temperature was defined by:

\[
\sigma_{i,T} = \sigma_{i,\text{ref}} (1 + \alpha(T - T_{\text{ref}})),
\]

where the reference temperature, \( T_{\text{ref}} \), was 300 K and the coefficient \( \alpha \) was 0.019 K\(^{-1}\), which was fitted using experimental data for 1 M sulfuric acid.\(^26\)

The temperature-dependent conductivity of the Nafion and the TCO layer was calculated by:

\[
\sigma_{\text{mem}/\text{TCO}, T} = \sigma_{\text{mem}/\text{TCO}, \text{ref}} \exp \left( \frac{E_{a,\text{mem}/\text{TCO}}}{RT_{\text{ref}}} \right) \times \exp \left( \frac{E_{a,\text{mem}/\text{TCO}}}{RT} \right),
\]

where \( \sigma_{\text{mem}/\text{TCO}, \text{ref}} \) is the Nafion/TCO conductivity at the reference temperature (300 K), \( E_{a,\text{mem}/\text{TCO}} \) is the activation energy for Nafion (set to 2000 J mol\(^{-1}\))\(^{27-28}\) and for TCO (set to 3185 J mol\(^{-1}\))\(^{29}\), respectively. The exchange-current density for the OER and HER, respectively, in the Butler-Volmer equation was defined using the activation energy \( E_{a,\text{OER}} \)\(^{30}\) and \( E_{a,\text{HER}} \)\(^{30}\):

\[
J_{0,\text{OER}} = J_{0,\text{ref}, \text{OER}} \exp \left( \frac{E_{a,\text{OER},\text{ref}}}{RT_{\text{ref}}} \right) \times \exp \left( \frac{E_{a,\text{OER}}}{RT} \right),
\]

\[
J_{0,\text{HER}} = J_{0,\text{ref}, \text{HER}} \exp \left( \frac{E_{a,\text{HER},\text{ref}}}{RT_{\text{ref}}} \right) \times \exp \left( \frac{E_{a,\text{HER}}}{RT} \right),
\]

Boundary conditions.— Boundary conditions that preserved the symmetry of the current density at the vertical walls were employed for both the trough and bubble wrap designs. Insulating boundary conditions were used at the upper and bottom bounds of the electrolyte domains. The current flux entering the TCO layers was calculated from the photovoltage using eq. 9. The electrochemical reactions for both designs were modeled as surface reactions occurring at the interface of the solution and the TCO layer. The ionic conductivities of the Nafion film and of 1 M H\(_2\)SO\(_4\) that were used in the modeling are listed in Table I. For the crossover calculation, the Dirichlet (or first-type) boundary condition was employed at the interfaces of the electrolyte and the TCO layers. The hydrogen (oxygen) concentrations at the
cathode (anode) were set to 0.78 mM (0 mM) and 0 mM (1.23 mM), respectively. Insulating boundary conditions for the product gas flux were also applied at the upper and lower bounds of the solution domains.

Free triangular discretization and a standard solver in the Comsol multi-physics package were used in the modeling. For both designs, the maximum and minimum mesh-element sizes were set to 10 μm and 0.5 μm, respectively. The maximum mesh-element growth rate and the resolution of curvature were set at 1.3 and 0.3, respectively. A relative tolerance of the corresponding variable of 0.001 was applied as the convergence criterion for both designs.

Operating principles of device efficiency.— The instantaneous STH conversion efficiency of an integrated photoelectrolysis device, \( \eta_{STH} \), was defined as:

\[
\eta_{STH} = \frac{F \cdot \Phi_0}{P \cdot \eta_{cell}},
\]

where \( J \) is the current density output from the device, \( \Phi_0 \) is the equilibrium potential of the electrochemical reaction, \( P \) is the input power of the solar energy, \( \eta_{cell} \) is the faradaic efficiency of the electroreaction, and \( \eta_{pc} \) is the product-collection efficiency. \( \eta_{cell} \) was set to unity in the model, while \( \eta_{pc} \) was defined by the following equation:

\[
\eta_{pc} = \frac{\int_{A_{anode}} j \, dA - \int_{A_{cathode}} nF \cdot \eta_{cell} \, dA}{\int_{A_{anode}} j \, dA},
\]

where \( j \) is the current density at the interfaces between the catalysts and the solution, the net reaction current, \( N_{cell} \), represents the current lost due to diffusive crossover of hydrogen from the cathode to the anode chamber, \( n \) is the number of electrons transferred (2 for the HER and 4 for the OER), \( A_{anode} \) and \( A_{cathode} \) are the electrode area and the Nafion area that separates the anodic and cathodic chambers, respectively.

To obtain a simple 0-dimensional analytical picture of the cell performance for diagnostic purposes, and therefore to aid in understanding the efficiency of the entire system at the individual-component level, the current-voltage characteristics of the cell, and the polarization curve for the water-splitting reaction, were typically overlaid to determine the operating current density.

Comparison to photovoltaic cell in series with an electrolyzer.— The STH efficiency of a stand-alone photovoltaic cell connected electrically in series with a discrete electrolyzer (PV + electrolyzer) was defined as,

\[
\eta_{STH} = \eta_{PV} \cdot \eta_{Electrolyzer} \cdot \eta_{DC-DC-converter},
\]

where \( \eta_{PV} \) is the solar-to-electricity conversion efficiency of the photovoltaic cell, \( \eta_{Electrolyzer} \) is the electricity-to-hydrogen conversion efficiency of the electrolyzer and \( \eta_{DC-DC-converter} \) is the efficiency of a DC-to-DC converter. The efficiency of the electrolyzer used for this comparison was the value optimized at a current density of 143.1 mV (Figure 3a) with the same electrode width, electrode and the two ends of the electrode increased from 6.5 mV to 49.4 mV respectively. The distribution of the current density along the electrode width also exhibited a strong position dependence. For example, Figure 3b shows the OER overpotential along the electrode for electrode widths of 10 μm, 1 mm, 3 mm and 5 mm, respectively. The distribution of the current density along the electrode width was highly non-uniform for this light-concentrating photoelectrolysis system. Compared to an unconcentrated system (data not shown), the OER overpotential difference between the mid-point and the two ends of the electrode increased from 6.5 mV to 49.4 mV (Figure 3b) and the maximum resistive loss increased from 17.2 mV to 143.1 mV (Figure 3a) with the same electrode width, electrode height and Nafion area (note that the areal Nafion coverage for the un-concentrated system is 10 times larger than for the system that utilizes solar concentration).

STH conversion efficiency.— The performance as a function of three important system-related geometric parameters: the electrode width or diameter; the electrode height; and the areal Nafion coverage of the entire cell, was evaluated systematically for both types of cell designs. The solution height was set to 5 mm (from the electrode to the upper or lower bound of the cell) so that the cell performance had a very weak dependence on the solution height. The detailed current density versus voltage characteristic of the tandem photoabsorbers was expected to have a significant impact on the overall value of \( \eta_{STH} \).
Ohmic losses associated with proton transport in the solution and in the membrane separator.—An efficient solar-to-fuel generator requires low (<100 mV) ohmic losses in the entire system.\(^7\) The ohmic loss is however highly dependent on the cell geometry. As shown in Figure 1c, both electrons and ions must be transported at steady-state from the anode/OER interface to the cathode/HER interface. Hence, the electronically conductive pathways occur from the oxygen-evolution catalysts through the TCO, the top cell, the bottom cell, and the second TCO, to the hydrogen-evolution catalysts. In contrast, the main ionically conductive pathways, that produce the predominant ohmic drop in the system, occur laterally from the oxygen-evolution catalysts (that are the site of proton production during current flow) in the top electrolyte to and through the surrounding membrane, and laterally in the bottom electrolyte to the hydrogen-evolution catalysts (that are the sites of proton consumption during current flow). Figures 5a and 5b, respectively show the ohmic loss calculated using system parameters that correspond to Figures 4(a)(i) and 4(b)(ii), respectively. To produce low ohmic losses in the trough design, the electrode width cannot exceed 2 mm, and the electrode height cannot exceed 40 μm (Figure 5a). The corresponding low ohmic loss criterion for the bubble-wrap design was satisfied when the electrode diameter did not exceed 3 mm and the electrode height did not exceed 50 μm (Figure 5b). Compared to the trough design, the same electrode dimensions in the bubble-wrap design resulted in less resistive loss due to improved radial transport of ion species in the electrolyte. Interestingly, a very small Nafion coverage (0.2%) could produce an ohmic resistive loss of <100 mV in a bubble-wrap cell with an electrode diameter as large as 2 mm.

Effect of catalysts.—The 10x concentrator design will operate at a higher current density (∼10x higher on average) than an un-concentrated system, so the kinetic overpotentials for HER and OER may be more critical to the overall \( \eta_{\text{STH}} \) in concentrated designs than in systems that do not utilize solar concentration. Figure 6 compares \( \eta_{\text{STH}} \) for both pairs of catalysts under detailed-balanced conditions at 300 K. For small electrode sizes (electrode width <600 μm and electrode height <10 μm for the trough design or electrode diameter <1 mm and electrode height <20 μm for the bubble-wrap design) \( \eta_{\text{STH}} \) was essentially unchanged (<3 percentage-point difference) when the different electrocatalysts were used, because the water-splitting polarization and photodiode behavior crossed at the plateau of the current density versus voltage curve, where the operating current density remained nearly constant. As the electrode width increased, \( \eta_{\text{STH}} \) exhibited a stronger geometric dependence on the properties of the electrocatalysts. For instance, for the large electrode (\( l = 1 \text{ cm} \) , \( h_e = 1 \text{ μm} \) and \( \xi = 0.2\% \) ) in the trough design, \( \eta_{\text{STH}} \) decreased from 22.1% to 7.3% when the “No. 1” catalyst pair was exchanged for the “No. 2” catalyst pair. The 0-dimensional analysis in Figure 2 illustrated the situation in which \( \eta_{\text{STH}} \) was strongly dependent on the catalyst activities at large electrode dimensions.

Effect of operating temperature.—Figure 7 shows \( \eta_{\text{STH}} \) for the systems at operating temperatures of 300 K and 350 K, respectively, with various combinations of the geometric parameters and with the photoabsorbers assumed to operate at the Shockley-Queisser detailed-balance limit. Two geometric regions, that exhibited opposite dependences of \( \eta_{\text{STH}} \) vs \( T \), were observed in the simulations. Figures 7a (iii) and 7b (iii) show, for both designs, the difference between \( \eta_{\text{STH}} \) at 350 K and \( \eta_{\text{STH}} \) at 300 K. When the solution transport and kinetic overpotential losses were small (i.e. at small electrode dimensions, and with a large Nafion coverage), \( \eta_{\text{STH}} \) decreased with increased operating temperature. For example, \( \eta_{\text{STH}} \) decreased from 26.7% to 25.5% for an electrode that was 10 μm wide and 1 μm thick when the Nafion coverage was 1% in the trough design (and from 26.7% to 25.5% for an electrode with a diameter of 10 μm and 1 μm thick when the Nafion coverage was 1% in the bubble-wrap design). In this geometric region, the decrease of \( \eta_{\text{STH}} \) with increasing \( T \) was dominated by the degradation of the performance of the light absorbers as \( T \) increased. In contrast, when the solution-transport loss and the kinetic

---

**Figure 3.** (a) Electrolyte potential-distribution profile for a “trough” design, with the electrode width, electrode height, solution height and Nafion coverage set to 3 mm, 10 μm, 5 mm and 1%, respectively. The black line represents the photocathode and photoanode assembly and the red lines represent the Nafion film. The streamlines represent the electrolyte current density. (b) The OER overpotential as a function of the normalized electrode width for a “trough” design with four electrode widths: 10 μm (black), 1 mm (red), 3 mm (green) and 5 mm (blue) under detailed-balance conditions at 350 K.
Figure 4. $\eta_{\text{STH}}$ calculated for the “trough” design (a) and for the “bubble wrap” design (b) as a function of the electrode width/diameter, $l/d_e$, the electrode height, $h_e$, and the Nafion coverage, $\xi$, for the tandem photoabsorbers at 350 K with a fill factor of 0.65 (i), 0.75 (ii) and at the detailed-balance limit (iii). The electrode width/diameter, $l/d_e$, was varied from 10 $\mu$m to 1 mm, with an interval of 150 $\mu$m, as well as from 1 mm to 1 cm, with an interval of 1 mm. The electrode height, $h_e$, was set from 1 $\mu$m to 100 $\mu$m, with an interval of 10 $\mu$m. The Nafion coverage, $\xi$, was set from 0.2% to 1%, with an interval of 0.2.

Overpotential losses were large (i.e. at large electrode dimensions and with a small Nafion coverage), $\eta_{\text{STH}}$ increased as $T$ increased. For example, $\eta_{\text{STH}}$ increased from 8.9% to 10.2% with a 1 cm electrode width, 100 $\mu$m electrode height and 0.2% Nafion coverage for the trough design (and from 10.6% to 11.7% with 1 cm electrode diameter, 100 $\mu$m electrode height and 0.2% Nafion coverage for the bubble-wrap design). In this geometric region, the increase of the $\eta_{\text{STH}}$ was dominated by enhanced rate of electrocatalysis as well as by enhanced solution transport as the temperature increased.

Comparison to a solar-hydrogen generator without a solar concentrator.— While a significant reduction of materials usage in solar concentrator-coupled photoelectrochemical cells is advantageous compared to cells without solar concentration, higher operating current densities in the concentrator design would result in higher catalytic overpotentials and higher transport loss and thus would lower the STH conversion efficiency of the cell. Figure 8 shows $\eta_{\text{STH}}$ of an unconcentrated cell system and of the 10x “trough” design, with identical cell geometries for the tandem photoabsorbers, at different
bandgap combinations. With the optimized cell geometry and active catalysts (“No. 1” catalyst system), $\eta_{\text{STH}}$ exhibited little change between the 10× the concentrated and unconcentrated systems. However, when the cell geometry was not optimized, a significant decrease in $\eta_{\text{STH}}$ and a significant difference in the bandgap combination dependence of the cell efficiency were observed. A similar change in $\eta_{\text{STH}}$ as a function of the bandgap combination was also observed in the “bubble-wrap” design. When the state-of-the-art catalyst system was used and the cell geometry was optimized, $\eta_{\text{STH}}$ in both the concentrated and unconcentrated systems were not limited by the electrocatalysis or the solution resistive loss. As a result, no significant difference in $\eta_{\text{STH}}$ was found between the two systems. However, when the resistive loss or electrocatalysis became the limiting factor in the system, a notable change in $\eta_{\text{STH}}$ was calculated between the

---

**Figure 5.** The geometric regions (electrode width, height and Nafion coverage) that maintained a low resistive loss (< 100 mV) in the “trough” design (a) and in the “bubble wrap” design (b).

**Figure 6.** $\eta_{\text{STH}}$ for the trough (a) and bubble-wrap (b) designs with the “No. 1” catalyst system (i) and the “No. 2” catalyst system (ii).
Figure 7. $\eta_{\text{STH}}$ at 300 K (i) and 350 K (ii) and the STH conversion-efficiency difference in percentage points (iii) for the trough (a) and the bubble-wrap (b) designs.

two systems. From the simulation, the concentrated system exhibited a stronger dependence on the cell geometry than the unconcentrated system.

Comparison to a standalone PV + electrolyzer design.—Figure 8 shows $\eta_{\text{STH}}$ of a stand-alone PV + electrolyzer system (c) and of the integrated 10x “trough” design with an optimal geometry (b) as a function of different bandgap combinations at 350 K. In both systems, state-of-the-art catalysts (“No. 1” catalyst system) were assumed. The highest value of $\eta_{\text{STH}}$ for the PV + electrolyzer system was 25.9%, when the top material had a 1.6 eV bandgap and the bottom material had a bandgap of 0.9 eV. For comparison, when the cell geometry was optimized, the integrated “trough” design exhibited $\eta_{\text{STH}} = 29.8\%$ at the same bandgap combination. A similar enhancement of $\eta_{\text{STH}}$ was also observed in the “bubble-wrap” design (Fig. 8b). These $\eta_{\text{STH}}$ values are almost identical to the optimized instantaneous $\eta_{\text{STH}}$ values for an integrated PEC system at 1 Sun (Fig. 8a). These 10x concentrator designs should therefore be considered as viable alternatives to “flat plate” designs that have been evaluated previously which utilize unconcentrated sunlight.

The higher currents in the 10x concentrator system increased the ohmic loss and also stressed the catalyst performance. However, the modeling described herein revealed that optimized cell designs, with the critical dimension of the photoelectrodes being less than a few millimeters, can result in very high STH conversion efficiencies, with $\eta_{\text{STH}} = 29.8\%$ (Fig. 8b). These $\eta_{\text{STH}}$ values are almost identical to the optimized instantaneous $\eta_{\text{STH}}$ values for an integrated PEC system at 1 Sun (Fig. 8a). These 10x concentrator designs should therefore be considered as viable alternatives to “flat plate” designs that have been evaluated previously which utilize unconcentrated sunlight.

The millimeter electrode length scale indicated by the modeling and simulation to be required for optimum $\eta_{\text{STH}}$ with 10x solar concentration could be readily implemented in a practical electrode manufacturing and cell assembly process. Moreover, the reduction of the materials usage for the photoelectrode (10% of the system area) and the Nafion (< 1% of the system area) would significantly reduce the cost of these potentially expensive components of a whole, scalable, solar fuels generation system. Large areas of insulating plastic (~90% of the system area) and the

Discussion

The higher currents in the 10x concentrator system increased the ohmic loss and also stressed the catalyst performance. However, the modeling described herein revealed that optimized cell designs, with the critical dimension of the photoelectrodes being less than a few millimeters, can result in very high STH conversion efficiencies, with $\eta_{\text{STH}} = 29.8\%$ (Fig. 8b). These $\eta_{\text{STH}}$ values are almost identical to the optimized instantaneous $\eta_{\text{STH}}$ values for an integrated PEC system at 1 Sun (Fig. 8a). These 10x concentrator designs should therefore be considered as viable alternatives to “flat plate” designs that have been evaluated previously which utilize unconcentrated sunlight.

The millimeter electrode length scale indicated by the modeling and simulation to be required for optimum $\eta_{\text{STH}}$ with 10x solar concentration could be readily implemented in a practical electrode manufacturing and cell assembly process. Moreover, the reduction of the materials usage for the photoelectrode (10% of the system area) and the Nafion (< 1% of the system area) would significantly reduce the cost of these potentially expensive components of a whole, scalable, solar fuels generation system. Large areas of insulating plastic (~90% of the system area) and the
dependence of at elevated temperatures the degradation of the performance of the PV electrodes in the system. Specifically, for small electrode dimensions, temperature is increased depend strongly on the dimensions of the enhancement of the solution transport and electrocatalysis as the trade-offs between the degradation of the PV performance and materials dominates the entire cell performance (Figure 7). However, for large electrode dimensions, under 10× concentration, the reduction of the ohmic loss and catalytic overpotentials improves ηSTH for the designs evaluated herein (Figure 7).

In both of the simulated designs, a 500 nm thick TCO layer having a sheet resistance of 20 Ω/□ was applied on the top and the bottom of the photoabsorbers. This laterally conductive TCO layer facilitated a redistribution of current along the electrode width and reduced the ohmic loss in the system (Figure 3). In optimized cell designs, in which the electrode dimension is less than a few millimeters, ohmic loss in the system (Figure 3). In optimized cell designs, in which the electrode dimension is less than a few millimeters, ηSTH was relatively insensitive to the presence or absence of the TCO layer. However, ηSTH would be lowered by 1.0 percentage points for a large “trough” design (l_e = 1 cm, h_e = 100 μm, ξ_e = 0.2%) at 350 K. ηSTH as a function of different bandgap combinations for a stand-alone PV+electrolyzer system (e) operating at 350 K. The “No. 1 catalyst system” was employed in all calculations.

The temperature profile of an actual operating system is highly dependent on the detailed construction of the cell, such as the particular encapsulation materials. Preliminary modeling results have suggested that a solar fuels generator system could operate at an elevated temperature (~330–350 K) without using an active cooling system. However, the 10× concentrator designs exhibit a stronger temperature dependence of ηSTH than systems that do not use solar concentration. The trade-offs between the degradation of the PV performance and the enhancement of the solution transport and electrocatalysis as the temperature is increased depend strongly on the dimensions of the electrodes in the system. Specifically, for small electrode dimensions, at elevated temperatures the degradation of the performance of the PV.

In operation, the system will likely be tilted at some angle relative to the surface normal. However, the light absorption, carrier transport, electrocatalysis and solution transport analyzed herein within the constraints of the present model are not expected to be sensitive to the tilt angle of the system itself. Gas evolution and thermal lift would be expected to enhance the convective mass transport in the solution, but a through evaluation of these features of an operating system will require development of operational prototypes and comparison with a more complete model of such a system. Moreover, the choice of different levels of the tracking system (truly stationary, occasional tilt adjustment tracking or active diurnal tracking) is likely to be determined by the trade-off between the balance of systems cost and the efficiency of the solar concentrator, which is beyond the scope of this work.

The temperature profile of an actual operating system is highly dependent on the detailed construction of the cell, such as the particular encapsulation materials. Preliminary modeling results have suggested that a solar fuels generator system could operate at an elevated temperature (~330–350 K) without using an active cooling system. However, the 10× concentrator designs exhibit a stronger temperature dependence of ηSTH than systems that do not use solar concentration. The trade-offs between the degradation of the PV performance and the enhancement of the solution transport and electrocatalysis as the temperature is increased depend strongly on the dimensions of the electrodes in the system. Specifically, for small electrode dimensions, at elevated temperatures the degradation of the performance of the PV...
stage of development of the type of integrated solar fuels generators evaluated herein.

A stand-alone PV+electrolyzer unit could in principle utilize a high-efficiency triple junction photovoltaic device, which can theoretically produce >40% energy-conversion efficiency. The optimal band gaps, and operating voltages, of such triple junctions are significantly larger than the optimal values for use in an integrated solar-driven water splitting system, which is more well-suited to the use of tandem structures. An optimally performing triple-junction stand-alone PV+electrolyzer system would therefore clearly outperform the optically performing tandem-based integrated solar fuels generators considered herein. For comparison of both types of tandem-based systems, ηTH for the PV+electrolyzer is obviously dependent on the efficiency of the DC-to-DC converter as well as the efficiency of the stand-alone electrolyzer unit. For optimal performance, the stand-alone system would require a DC-DC converter that dynamically tracks the maximum power point of the PV array, and that also dynamically adjusts its output voltage and current to maintain optimal performance of the electrolyzer unit. Comparison of the data of Figures 4, 6 and 8, along with a linear increase of the efficiencies depicted in Figure 8 by higher assumed efficiencies for the electrolyzer and for the DC-DC converter in the stand-alone PV+electrolyzer combination, indicates that the optimized integrated system can in fact, with the physical electrode dimensions, membranes, electrolytes and system geometry described herein, provide comparable efficiency to that of an optimized, stand-alone PV+electrolyzer combination. The optimized 10× concentrator designs with smaller electrode dimensions described herein also permit the use of a semiconductor/liquid junction, in which no “buried” junction or lateral conductive TCO layer is required. The ability to utilize a stable semiconductor/liquid junction in the integrated design, e.g., a metal oxide/OER junction, would significantly broaden the materials choices relative to that available at present for a discrete PV unit, in which a solid-state “buried” junction is required.

Conclusions

In an integrated photoelectrolysis system that does not utilize solar concentration, maintaining low ohmic losses requires a maximum electrode width less than a few centimeters. In contrast, to maintain comparable ohmic losses, the integrated 10× concentrated devices modeled in this work that require the maximum electrode width or diameter must remain on the order of a few millimeters. The distribution of current density along the electrode width was observed to be nonuniform for the 10× concentrator designs, particularly for large cell dimensions. The overall ηTH of systems with smaller electrode dimensions showed a weaker dependence on the performance of the photoabsorbers and the catalysts than was the case for cells with larger dimensions. Minimal coverage of Nafion (<1% of the cell area) was needed to maintain an ohmic loss of <100 mV in the bubble-wrap cell at the operating temperature of 350 K, with an electrode diameter and height as large as 2 mm and 1 μm, respectively. With the same Nafion coverage and electrode height, when the electrode width in the trough design equalled the electrode diameter in the bubble-wrap design, the bubble-wrap design exhibited higher ηTH due to enhanced radial solution transport. At elevated operating temperatures, ηTH of cells with smaller dimensions decreased due to degradation of the performance of the photoabsorber materials, while ηTH of cells with larger dimensions increased with temperature due to enhanced transport in the solution and enhanced catalytic activity. The simulations also indicated that both optimized 10× concentrator designs (having small electrode dimensions) yielded comparable performance to an optimized PV + electrolyzer system, validating the merit of considering such integrated designs for implementation of a solar fuels generator that minimizes the materials utilization of the light absorbers and ionically conductive membranes in the system.

Acknowledgments

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. The authors thank John C. Stevens for helpful discussion regarding the optics of solar concentrator designs. Authors Yikai Chen and Chengxiang Xiang contributed equally to this work.

References

1. Basic research needs for solar energy utilization, U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Washington, D.C. (2005).
2. N. S. Lewis, Science, 315, 798 (2007).
3. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. X. Mi, E. A. Santori, and N. S. Lewis, Chem Rev., 110, 6446 (2010).
4. A. J. Bard and M. A. Fox, Accts. Chem. Res., 28, 141 (1995).
5. B. A. Pinaud, J. D. Benck, L. C. Seitz, A. J. Forman, Z. B. Chen, T. G. Deutsch, B. D. James, K. N. Baum, G. N. Baum, S. Ardo, H. L. Wang, E. Miller, and T. P. Jaramillo, Energ Environ Sci, 6, 1983 (2013).
6. B. D. James, G. N. Baum, J. Perez, and K. N. Baum, Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production in, Directed Technologies (2009).
7. G. Peharz, F. Dimroth, and U. Wittstätt, Int. J. Hydrogen Energy, 32, 3248 (2007).
8. D. J. Friedman, R. R. King, R. M. Swanson, J. McManness, and D. Gwinner, IEEE J Photovoltol, 3, 1460 (2013).
9. D. C. Miller and S. R. Kurtz, Sol. Energy Mater. Sol. C, 95, 2037 (2011).
10. A. Luque, J Appl Phys, 110, 031301 (2011).
11. R. Winston, J. C. Miñano, and P. G. Benitez, Nonimaging optics, Academic Press (2005).
12. J. J. O’Gallagher, Synthesis Lectures on Energy and the Environment: Technology, Science, and Society, 2, 1 (2008).
13. J. C. Stevens and A. Weber, Manuscript in preparation (2014).
14. J. Turner, Nat. Mater., 7, 770 (2008).
15. B. Parkinson, Sol. Cells, 6, 177 (1982).
16. S. Haussener, S. Hu, C. X. Xiang, A. Z. Weber, and N. S. Lewis, Energ. Environ. Sci., 6, 3603 (2013).
17. S. Haussener, C. X. Xiang, J. M. Spurgeon, S. Ardo, N. S. Lewis, and A. Z. Weber, Energ. Environ. Sci., 5, 9922 (2012).
18. S. Hu, C. X. Xiang, S. Haussener, A. D. Berger, and N. S. Lewis, Energ. Environ. Sci., 6, 2984 (2013).
19. J. M. Gregoire, C. X. Xiang, X. N. Liu, M. Marcini, and J. Jin, Rev Sci. Instrum., 84 (2013).
20. S. M. Sze, Physics of Semiconductor Devices, John Wiley & Sons, New York (1981).
21. A. J. Bard and L. R. Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley (2000).
22. S. Haussener, C. X. Xiang, J. M. Spurgeon, S. Ardo, N. S. Lewis, and A. Z. Weber, Energ. Environ. Sci., 5, 9922 (2012).
23. A. Rabl, Sol. Energy, 18, 93 (1975).
24. W. Shockley and H. J. Queisser, J. Appl Phys., 32, 510 (1961).
25. C. H. Henry, J. Appl. Phys., 51, 4494 (1980).
26. H. E. Darling, Journal of Chemical & Engineering Data, 9, 421 (1964).
27. H. Ito, T. Maeda, A. Nakano, and H. Takenaka, Int. J. Hydrogen Energy, 36, 10527 (2011).
28. Y. Sone, P. Ekdunge, and D. Simonsson, J. Electrochem. Soc., 143, 1254 (1996).
29. J. George and C. Menon, Surface and Coatings Technology, 132, 45 (2000).
30. K. Kinoshita, Electrochemical Oxygen Technology, New York: Wiley (1992).
31. N. Markovic, B. Grup, and P. Ross, J. Phys. Chem. B, 101, 5405 (1997).
32. W. Sheng, H. A. Gastegier, and Y. Shao-Horn, J. Electrochem. Soc., 157, B1529 (2010).
33. S. Sirlacusan, V. Baglio, A. Di Blassi, N. Briguglio, A. Stassi, R. Ornelas, E. Trifoni, V. Antonucci, and A. Arico, Int. J. Hydrogen Energy, 35, 5558 (2010).
34. A. T. Marshall, S. Sunde, M. Tsyarkin, and R. Tunold, Int. J. Hydrogen Energy, 32, 2320 (2007).
35. F. Barbir, Sol. Energy, 78, 661 (2005).
36. J. Ivy, Summary of Electrolytic Hydrogen Production: Milestone Completion Report, p. Medium: ED; Size: 28 pp; pages (2004).
37. J. Newman, P. G. Hoertz, C. A. Bonino, and J. A. Trainham, J. Electrochem. Soc., 159, A1722 (2012).