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Modeling integrated photovoltaic–electrochemical devices using steady-state equivalent circuits

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We describe a framework for efficiently coupling the power output of a series-connected string of single-band-gap solar cells to an electrochemical process that produces storable fuels. We identify the fundamental efficiency limitations that arise from using solar cells with a single band gap, an arrangement that describes the use of currently economic solar cell technologies such as Si or CdTe. Steady-state equivalent circuit analysis permits modeling of practical systems. For the water-splitting reaction, modeling defines parameters that enable a solar-to-fuels efficiency exceeding 18% using laboratory GaAs cells and 16% using all earth-abundant components, including commercial Si solar cells and Co- or Ni-based oxygen evolving catalysts. Circuit analysis also provides a predictive tool: given the performance of the separate photovoltaic and electrochemical systems, the behavior of the coupled photovoltaic–electrochemical system can be anticipated. This predictive utility is demonstrated in the case of water oxidation at the surface of a Si solar cell, using a Co–borate catalyst.

Powering electrochemical reactions with photovoltaic devices to produce fuels provides an appealing solution to the societal need for clean energy (1). Although the deployment of photovoltaic modules has expanded rapidly over the last decade as costs have dropped (2), utilization of solar power is constrained by its local intermittency, thus providing an imperative for storage by the direct conversion of solar energy to chemical fuels. Photosynthetic organisms directly convert solar energy into chemical fuels by splitting water to produce molecular oxygen and hydrogen equivalents, which are fixed by their combination with carbon dioxide to produce carbohydrates. The technological imitation of photosynthesis—an “artificial leaf”—can be realized by integrating oxygen and hydrogen evolution catalysts to a semiconductor in a buried junction configuration (3). Most buried junction devices have relied on expensive solar cell architectures and/or catalysts (4), including those demonstrating solar-to-fuels efficiencies (SFEs) exceeding 18% (5–7). More economical artificial leaves have been realized with earth-abundant catalysts and solar cell materials but at reduced SFE (8, 9). We now seek to provide an analytical framework for the construction of higher SFE architectures comprising earth-abundant materials.

The efficiency of converting solar energy to stored chemical fuel has been considered (10–13) for a variety of configurations, including the specific treatment of buried junction devices (10). A primary result of these analyses is that single-junction solar cells are limited in powering water splitting with high SFE because solar cell materials that are well matched to the solar spectrum do not produce sufficient voltages to drive water splitting. Multijunction devices overcome this limitation, enabling high SFE by integrating several materials into a single multijunction device (5–7, 12). Despite their higher limiting SFEs, however, multijunction devices are costly; thus single-junction devices with higher SFEs would be preferred.

To this end, we explore in this contribution strategies to maximize the SFEs of designs, using a single absorber material. Whereas a single absorber is often unable to generate sufficient voltage to drive water splitting, arranging solar cells in series can increase voltage and produce higher SFE. We describe the efficiency limitations faced by series-connected devices, emphasizing the fundamental efficiency-limiting role played by electrical coupling between the electrochemical and photovoltaic processes. In addition, we introduce a framework for modeling practical photovoltaic–electrochemical (PV-EC) devices and use it to analyze the design requirements for water splitting using series-connected Si solar cells. We focus on Si due to its lower cost and overwhelming market advantage (2). We develop the steady-state equivalent circuit (i.e., neglecting reactive elements) of a coupled PV-EC system and use it to demonstrate two important design capabilities. First, equivalent-circuit analysis enables modeling of realistic PV-EC systems. Consequently, it describes the impact of key parameters such as the Tafel slope of the catalysts, the diode ideality of the PV device, and the series and solution resistance of the PV and EC systems, respectively. Second, the performance of the coupled PV-EC system can be predicted via separate characterization of the PV device and the EC cell. We illustrate this capability using a practical PV-EC device (Si integrated with recently discovered Co-OEC (14–16) and Ni-OEC (17, 18) catalysts). We show that practical PV-EC devices using commercial Si solar cells and earth-abundant catalysts should be capable of yielding SFEs comparable to those of multijunction solar cells.

Results and Discussion

Device Construct. Fig. 1A illustrates a PV-EC using a PV, an electrochemical system, and a coupling system. The coupling system matches the electrical output (current and voltage) of the PV device to the electrical input of the EC process. In this arrangement, the steady-state efficiency $\eta_{\text{SF}}$ with which solar power is transferred to chemical fuels is given by:

$$\eta_{\text{SF}} = \frac{P_{\text{EC}}}{P_{\text{PV}}}$$

where $P_{\text{EC}}$ is the electrical power output of the EC device and $P_{\text{PV}}$ is the electrical power output of the PV device.

This article extends the construction of direct solar-to-fuels devices, such as the artificial leaf based on crystalline silicon. Because a single Si junction has insufficient potential to drive water splitting, it cannot be used for direct solar-to-fuels conversion. This paper performs an equivalent circuit analysis for multiple series-connected devices. The predictive utility of the model is demonstrated in the case of water oxidation at the surface of a Si solar cell, using a cobalt–borate oxygen evolving catalyst. Considering recent cost reductions of Si solar cells, this paper offers a path to the construction of low cost solar-to-fuels devices.

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The efficiency $\eta_{pv}$ of a solar cell is thermodynamically limited. The maximum efficiency varies as a function of the absorber’s band gap $E_g$ and exhibits a broad efficiency maximum of about 30% (20) near $E_g \sim 1.2$ eV. Although this is near the water-splitting potential, a solar cell’s maximum voltage is thermodynamically limited to be 300–400 mV lower than $E_g/4$ at room temperature (21). Technologically, these thermodynamic limits are approached only by mature materials such as Si and GaAs (22). The maximum voltage and current of a cell are measured under open- and short-circuit conditions and are referred to as $V_{oc}$ and $J_{sc}$, respectively. The maximum power output of a solar cell occurs at a current $J_{mp}$ and voltage $V_{mp}$ smaller than these maximum values and is often expressed as $FF \times J_{sc}V_{oc}$, with the fill factor, $FF = J_{mp}V_{mp}/J_{sc}V_{oc}$. The fill factor is thermodynamically limited to be in the range 0.8–0.9 for most materials of interest (21), but imperfections such as series resistance (see Eq. 7 or Fig. 34) yield lower values. Given the solar irradiance $P_{sun}$, the efficiency of a solar cell is thus

$$\eta_{pv} = \frac{FF \times V_{oc} \times J_{sc}}{P_{sun}}. \quad [2]$$

When $N$ identical solar cells are connected in series, their output voltages sum while the current density decreases as $1/N$. (If cells are arranged next to each other in a plane perpendicular to the incident light, total current is constant but area grows as $N$. Alternatively, the cells can be arranged along the direction of incident light propagation as in ref. 8. In this case, the area presented to incident light remains constant, each cell absorbs only a fraction of the incident light, and total current drops as $1/N$. In both cases, current density drops as $1/N$.) In practice, variations in cell-to-cell performance will reduce the overall efficiency of the series-connected cells; such “mismatch losses” are not explicitly considered in Eq. 2.

The efficiency $\eta_{ec}$ of an electrochemical process is generally dominated by kinetic limitations rather than thermodynamic ones. The operating voltage $V_{op}$ must exceed the thermodynamic potential $\mu_{th}$ to achieve a sufficient reaction rate or operating current density $J_{op}$. For a fuel-generating reaction, the power flow into the stored chemical energy is $\mu_{th}J_{op}$ whereas the total electrical energy dissipated is $V_{op}J_{op}$. Thus, the efficiency of the electrochemical reaction is

$$\eta_{ec} = \frac{\mu_{th}}{V_{op}}. \quad [3]$$

In the case of the water-splitting reaction, the oxygen evolution reaction (OER) occurs at the anode and the hydrogen evolution reaction (HER) occurs at the cathode. The HER can be catalyzed at low overpotentials relative to the OER; thus this efficiency is usually dominated by the choice of OER catalyst (23). At the current densities necessary for a PV-EC device, earth-abundant catalysts provide OER overpotentials that range from 0.25 to 0.4 V, corresponding to $\eta_{ec}$ in the range of 75–85%. Lower overpotentials are possible with non-earth-abundant materials such as RuO$_2$ (4).

The efficiency $\eta_{c}$ of the coupling system is entirely dependent on the choice of implementation, and its efficiency is not limited by any fundamental consideration. In principal, the simplest way to couple the systems may be to perform the anodic and cathodic reactions on the positive and negative terminals of a buried junction (or series of solar cells), respectively. In the case of water splitting, this geometry is sometimes referred to as an artificial leaf (3). We refer to this coupling scheme, or any other in which the two half-reactions occur on surfaces equipotential with the terminals of a solar cell, as direct electrical connection; it describes both wired and wireless water splitting (Fig. 1B). Fig. 1A illustrates that direct electrical connection is equivalent to constraining the currents and voltages of the PV device and the EC system to be identical: $J_{pv} = J_{ec}$ and $V_{pv} = V_{ec}$. Graphically, this constraint identifies the operational state of the coupled PV-EC device as the point at which the steady-state current–voltage properties of the PV device and the EC system intersect (24). This mode of operation may result in the solar cell producing less...
than its maximum output \( V_{\text{op}}J_{\text{op}} < V_{\text{mp}}J_{\text{mp}} \). Referring to Eq. 2, the coupling efficiency is

\[
\eta_c = \frac{V_{\text{op}} \times J_{\text{op}}}{FF \times V_{\text{oc}} \times J_{\text{sc}}},
\]

[4]

Alternatives to direct coupling are also possible. For example, power electronics could convert the electrical output of one or more solar cells to the required electrical input of the electrochemistry. Practically, the choice of a coupling scheme would be dictated by matching the tolerable complexity, reliability, and cost of an application with available coupling solutions.

Using the above expressions, Eq. 1 can be rewritten as

\[
\eta_{\text{SF}} = \frac{FF \times V_{\text{oc}} \times J_{\text{sc}}}{P_{\text{sun}}} \frac{\mu_{\text{th}}}{V_{\text{op}} \times J_{\text{op}} \times FF \times V_{\text{oc}} \times J_{\text{sc}}} = \frac{\mu_{\text{th}} \times J_{\text{op}}}{P_{\text{sun}}}.\]

[5]

The final term of Eq. 5 represents the SFE of an electrochemical reaction driven by solar power. In Fig. 1C, we summarize each of these efficiency terms graphically. We note that, because the HER occurs on the negative terminal of the solar cell, the x axis of Fig. 1C is referenced to a reversible hydrogen electrode (RHE) and is thus invariant with pH.

We consider the scenario in which only a single type of PV absorber is used. Single-absorber technologies compose the vast majority of the terrestrial PV market (25), so it seems likely that deployment of PV-EC devices, at a scale meaningful relative to the energy economy, would require the lowest-cost, most widely available solar cell technology. Currently, Si and CdTe dominate this category, although technologies such as Cu(In_{1-x}Ga_x)Se_2 and GaAs are also in commercial production (25). For single-absorber solar cells to generate a voltage sufficient to drive a reaction, several cells may have to be wired in series. For example, an outstanding Si solar cell produces a maximum voltage of about 700 mV (22). Thus, at least two cells, wired in series, would be required to drive the water-splitting reaction (\( \mu_{\text{th}} = 1.23 \) V). If an excess of cells were added in series, however, the operating point of the coupled PV-EC system would fall far from the maximum power point of the cell (Fig. 2B: e.g., note the intersection of the \( R_{\text{op}} = 0 \) electrochemical curve with the three- and four-cell curves).

Such analysis permits calculating the limiting efficiency for any electrochemical reaction powered by a single-absorber solar cell. First, the current density output \( J_{\text{op}} \) from a series arrangement of \( N \) ideal solar cells is calculated at the voltage equivalent to the thermodynamic potential of a reaction \( \mu_{\text{th}} \). The SFE is then calculated using Eq. 5. The number of cells \( N \) is chosen to maximize the SFE. The results of this calculation are shown in Fig. 2A. Because Fig. 2A represents ideal solar cells and electrochemistry, it primarily reflects the impact of direct electrical coupling on the thermodynamics of solar energy conversion. The high-contrast lines in Fig. 2A identify conditions at which the addition or subtraction of a cell dramatically changes the efficiency the PV-EC system. A representative scenario is shown in Fig. 2B (which illustrates coupling for the practical devices considered in Fig. 3B) at the point marked by the red asterisk. Although ideal PV and EC systems are used to generate Fig. 2A, the implication that impedance matching is critical for efficient operation of PV-EC devices is generalizable to nonideal cases. Practical cases are considered in PV-EC Equivalent Circuit and Device Modeling and this calculation is replicated with practical inputs in Fig. S1.

The maximum theoretical SFE for series-connected single absorbers is 30.8% and occurs for a solar cell with \( E_g = 1.38 \) eV. Because the calculation treats electrochemistry as ideal (\( \eta_{\text{ec}} = 1 \)), the optimal efficiency and band gap are identical to those for an ideal solar cell (21). Correspondingly, the only (ideal) electrochemical reactions that could be carried out at this efficiency would be those for which \( \mu_{\text{th}} \) is equal to the voltage at the maximum power point of the solar cell device (s). To obtain \( V_{\text{mp}} = \mu_{\text{th}} \) (and thus \( \eta_c = 1 \)), the reaction must occur at \( \mu_{\text{th}} = N \times 0.93 \) V, where \( N \) is an integer. For water splitting (\( \mu_{\text{th}} = 1.23 \) V), the maximum SFE is 27.5% and it occurs for two series-connected cells with \( E_g = 1.04 \) eV; the efficiency when Si (\( E_g = 1.12 \) eV) powers the reaction is only slightly smaller (\( \eta_{\text{SF}} = 26.9\% \)). Critically, we note that most materials well matched to the solar spectrum (1.0 eV < \( E_g < 2.0 \) eV) exhibit theoretical efficiencies at or above 20% provided that an appropriate number of cells are placed in series; some relevant technologies are shown in Table 1.

**PV-EC Equivalent Circuit and Device Modeling.** Solar cells and electrochemical reactions do not operate at thermodynamic limits. The electrical behavior of practical PV and EC systems can be described in steady state, using equivalent circuits (Fig. 3A). Circuit analysis enables accurate modeling of PV-EC devices and provides insight into their realistic performance and efficiency limitations.

The equivalent circuit of a PV device is well known (26). In a PV device, light absorption generates a current of excited

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Fig. 2. (A) Density plot of the efficiency of using the output power of an ideal solar cell (band gap \( E_g \)) to produce and store chemical energy via reversible electrochemical (EC) reactions (thermodynamic reaction potentials \( \mu_{\text{th}} \)). Considering only single-band-gap solar cells, EC reactions with \( \mu_{\text{th}} \) larger than solar cell operating voltages require multiple cells in series. The plot exhibits regions defined by the number of cells required for efficient coupling, characterized by band gap \( E_g \) to produce stored chemical energy via reversible EC reactions defined by thermodynamic reaction potentials \( \mu_{\text{th}} \). Because only single-band-gap solar cell materials are considered, EC reactions with \( \mu_{\text{th}} \) larger than the operating voltages of the solar cells (\( E_g / q = -350 \) mV, where \( q \) is the fundamental charge) require multiple cells in series. The plot is separated by areas of rapidly changing efficiency into regions defined by the number of solar cells required for efficient coupling. (B) Current density-voltage plot indicating the impact of electrochemical parameters on the coupling efficiency and the number of realistic Si solar cells (\( \eta_{\text{th}} = 20\% \)) required. Overlaid points correspond to solutions also shown in Fig. 3B.
Table 1. Theoretical limiting efficiency for common solar cell absorbers when powering ideal water splitting

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$/eV</th>
<th>$\eta_{th} \times 100%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si*</td>
<td>1.12</td>
<td>26.9</td>
</tr>
<tr>
<td>Cu(In$<em>{0.5}$Ga$</em>{0.5}$)Se$_2$</td>
<td>1.15$^2$</td>
<td>26.1</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>19.7</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.44</td>
<td>19.2</td>
</tr>
<tr>
<td>a-Si$^3$</td>
<td>1.7</td>
<td>26.8</td>
</tr>
</tbody>
</table>

*Crystalline silicon.

$^2$Band gap is representative of high-efficiency Cu(In$_{0.5}$Ga$_{0.5}$)Se$_2$ devices (32).

$^3$Amorphous silicon.

electrons and holes that relax by recombining, some by flowing through an external circuit with current density $J_{PV}$. Although a well-designed solar cell maximizes $J_{PV}$, some photogenerated carriers are lost to internal recombination via one or more recombination mechanisms. Each recombination current can generally be described by a diode equation,

$$J_n(V) = J_0 \left[ \exp \left( \frac{V}{nV_{th}} \right) - 1 \right] \approx J_0 \exp \left( \frac{V}{nV_{th}} \right).$$

where $J_0$ is the saturation current density that describes the equilibrium rate of the mechanism and $V_{th} = k_B T/q$ is the thermal voltage (given by the electron charge $q$, temperature $T$, and Boltzmann constant $k_B$). The approximation on the right side of Eq. 6 is accurate at typical solar cell operating voltages. The value of the ideality factor $n$ depends on the recombination mechanism, but the use of one or two recombination currents is often sufficient to provide an accurate description of most high-performance materials. Ohmic losses can be modeled by introducing a series resistance $R_s$ that modifies the output device voltage, and shunt paths that bypass the intended circuit can be approximated by a resistance $R_{sh}$. The output current density $J_{PV}$ is the difference between the generated photocurrent $J_L$ and the recombination currents,

$$J_{PV}(V) = J_L - J_{0,1} \exp \left( \frac{V + J_{PV} R_s}{n_1 V_{th}} \right) - J_{0,2} \exp \left( \frac{V + J_{PV} R_s}{n_2 V_{th}} \right)$$

Eq. 7 is represented using typical circuit components in Fig. 3A. If $N$ identical solar cells are wired together in series, their voltages are additive whereas the current density of the entire system will decrease as $1/N$. This feature can be approximated by defining $\eta_{PV} = J_{PV}(V)/N$.

An electrochemical reaction proceeds only when the voltage between two electrodes exceeds the thermodynamic potential $\mu_{th}$ of the reaction by an amount sufficient to drive the reaction kinetics. The voltage $V$ necessary to drive an electrochemical current density $J_{ec}$ is given by adding the thermodynamic potential, the overpotential for each reaction (given by the Tafel law), and the Ohmic losses to solution resistance $R_{sol}$. For the water-splitting reaction, the OER and the HER are the electrochemical reactions of interest, and the necessary voltage is given by

$$V = \mu_{th} + \tau_o \log \left( \frac{J_{ec}}{J_0} \right) + \tau_i \log \left( \frac{J_{ec} R_{sol}}{J_0} \right) + J_{ec} R_{sol}.$$  

In Eq. 8, the terms $\tau$ and $J_0$ are the Tafel slope and the exchange current density, respectively. The OER and the HER are each characterized by a distinct $\tau$ and $J_0$, identified in Eq. 8 by the superscripts “O” and “H”, respectively. The impact of these kinetic parameters has been explored in detail (24). For the purpose of completing the circuit diagram of the steady-state behavior of the PV-EC device, we note that the Tafel law is mathematically identical to the diode equation. For example, the current–voltage properties of the OER are given by

$$V_{OER} - V_{th}^0 = \tau_o \log \left( \frac{J_{ec}}{J_0} \right) + J_{ec} R_{sol}.$$  

where all parameters are as defined above, but in this case $V_{th}^0$ is the Nernstian potential for the OER. It is clear that Eq. 9 has the same form as the diode equation (Eq. 6) under the substitutions $V_{OER} \rightarrow V_{th}^0$, $V_{th} \rightarrow V_{th}^0$, and $J_0 \rightarrow J_0^0$. Thus, each electrochemical reaction can be represented as a diode operating under a reverse bias equal to the thermodynamic or Nernstian potential; this condition is represented in Fig. 3A.

The circuit shown in Fig. 3A can be solved to model the coupled PV-EC system. Under the constraint that $J_{ec} = J_{PV}$, Eqs. 7 and 8 can be solved numerically for the operational
voltage, current density, and resulting SFE (given a set of device characteristics for the PV device and the EC system). For example, assuming that the system is powered by high-performance, commercially available silicon solar cells ($\eta_{pv} = 20\%$), the behavior of the system under different electrochemical parameters can be explored along with the number of solar cells required to optimally couple the system. Fig. 3B illustrates the impact of solution resistance and OER Tafel slope (see Tables 2 and 3 for the parameters). OER catalysts produce different Tafel slopes depending on their mechanism; in this work, Tafel slopes of 120, 60, and 40 mV/decade are considered. In each scenario, the operating voltage and resulting efficiency are found when power is provided by an optimal number of $N$ identical solar cells wired in series.

To ensure optimal coupling, the value of $N$ changes depending on the performance of the rest of the system; for the range of parameters studied, anywhere between three and five cells are required. The points at which $N$ changes value are evident in Fig. 3B by kinks in the curve (for clarity, the efficiency for coupling to $N = 3$ is shown for all values of $R_{sol}$). Fig. 2B illustrates the graphical solution for several points on the curves in Fig. 3B (for $\tau_0 = 40$ mV/decade and $R_{sol} = 0$ and 60 $\Omega$-cm$^2$); these points are denoted in both figures by solid and open circles. For $R_{sol} = 0$, it is clear that three series-connected solar cells provide a higher operating voltage (at a nearly identical operating voltage) than a four-cell arrangement. For $R_{sol} = 60$ $\Omega$-cm$^2$, however, the overpotential increases significantly and requires four series-connected solar cells to achieve significant currents; Fig. 2B illustrates this fact at points marked by open red and solid red circles.

The SFE exceeds 15% provided a high-performance OER catalyst ($\tau_0 = 40$ mV/decade) and low solution resistance ($R_{sol} < 10$ $\Omega$-cm$^2$) are realized. SFE exceeds 10% for all but the least attractive electrochemical parameters studied ($\tau_0 = 120$ mV/decade and $R_{sol} > 40$ $\Omega$-cm$^2$), indicating that the low SFE observed for water splitting with earth-abundant materials stems from using low-efficiency solar cell devices (8, 27) and/or poor electrical coupling. Thus, a high-efficiency ($\eta_{pv} > 10\%$) PV-EC device should be feasible using entirely earth-abundant components operating at or near neutral pH. Appropriate catalysts have been demonstrated (14–18), and PV-device design can minimize $R_{sol}$. Given electrode spacing $d$ and solution conductivity $G$, Ohmic losses are $\Delta V = \eta_{oc} R_{sol} + J_{opt} d/G$. Thus, electrode geometry can minimize Ohmic losses even in relatively low conductivity solutions. Fig. 1B (Right) illustrates a design in which solar cells are coupled to the electrolyte via interdigitated contacts; using standard screen printing, electrode spacing could be reduced to $d < 100$ $\mu$m. For $J_{opt} \sim 15$ mA$\text{cm}^{-2}$ and $G = 50$ mS$\text{cm}^{-1}$ (achievable at neutral pH), Ohmic losses will be reduced to $\Delta V = 3$ mV. Treating this voltage drop as an increase in the overpotential, Eq. 3 indicates a negligible impact on SFE of $\sim0.2\%$ relative. In this geometry, however, $H_2$ and $O_2$ are proximately evolved, and crossover is minimized owing to the selectivity of the catalyst design (i.e., the OER catalysts do not oxidize $H_2$ because $H_2$ does not coordinate to CoNi-P/B. Oxidic clusters and vice versa $O_2$ reduction by the HER catalysts is minimal). In this design, however, $H_2$ and $O_2$ must be separated. This issue has been considered in the case of anodes and cathodes on separate surfaces within an electrochemical cell (28, 29), but would need to be readdressed for an interdigitated, coplanar geometry.

Although it is clear from Fig. 3B that better catalysis and lower solution resistance are desirable for higher SFE, Fig. 3B also illustrates the trade-offs when directly coupling a PV and EC system. In some scenarios, the quality of catalysis governs the efficiency. For example, given inefficient catalysis (Tafel slope of 120 mV/decade), SFE exceeding 10% is possible only if the optimal number of solar cells is wired in series ($N = 4$) and $R_{sol}$ is minimal. In this particular case, the coupling efficiency $\eta_{c} \sim 1$ and efficiency losses beyond those in the solar cell are governed by a high overpotential ($\sim1$ V), leading to $\eta_{oc} = 0.57$. Moreover, if only three solar cells are wired in series in this instance, the SFE is minimal due to extremely inefficient coupling: Even at $R_{sol} = 0$, the system efficiencies are ($\eta_{pv}, \eta_{oc}, \eta_{ec} = (0.20, 0.09, 0.62)$. For 60- and 40-mV/decade catalysis, on the other hand, SFEs approaching or exceeding 15%, respectively, are possible. For a system with low $R_{sol}$ coupling is almost perfect (Fig. 2B, solid red circle), and losses beyond those of the PV device originate only from the small overpotential [for 40 mV/decade at $R_{sol} = 0$, ($\eta_{pv}, \eta_{oc}, \eta_{ec} = (0.20, 1.00, 0.76)$]. Fig. 3B emphasizes that achieving high SFE relies on many interdependent factors.

We distill from these analyses several design guidelines for PV cells used in a PV-EC system. First, increasing the current of a PV device will always produce a proportionate increase in SFE, whereas an increased voltage will not. This observation is evident from Eq. 5, and Fig. S2 clarifies this point graphically. One consequence of this observation is that higher-efficiency solar cells do not always provide a proportionate increase in the solar-to-fuels efficiency. For example, the most efficient Si solar cell in commercial production has an efficiency $\eta_{oc} = 23.6\%$ (30); however, it achieves this efficiency through higher voltages ($V_{oc} = 727$ mV) rather than higher currents ($J_{sc} = 40$ mA$\text{cm}^{-2}$), relative to the 20% cell modeled above. As a result, $\eta_{pv}$ increases only by about 6% relative (from 15.3 to 16.3%). This increase is due to moving the operating point closer to short-circuit conditions (emphasized in Fig. S2). Similarly, modeling the highest-efficiency single-junction solar cell ever produced [a GaAs solar cell with $\eta_{oc} = 28.8\%$ (22)] increases $\eta_{oc}$ to an impressive 18.2%, but this SFE still underperforms the improvement in PV efficiency significantly. An underlying reason for this is that the cell voltage ($V_{oc} = 1.12$ V) couples less efficiently to the water-splitting reaction ($\eta_{oc} = 0.83$). We elaborate on both of these examples in Figs. S1–S3.

The second design guideline is that the sensitivity of the PV-EC system to solution resistance is highly dependent on conditions of coupling: namely, if a system is not optimally coupled, it may be relatively insensitive to changes in solution resistance. This observation is clear in Figs. 2B and 3B and particularly evident in Fig. S3. The optimal coupling for OER I conditions

<table>
<thead>
<tr>
<th>OER kinetics</th>
<th>Tafel slope, mV/decade</th>
<th>Exchange current density, mA$\text{cm}^{-2}$</th>
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<tbody>
<tr>
<td>Case I</td>
<td>40</td>
<td>$5 \times 10^{-12}$</td>
</tr>
<tr>
<td>Case II</td>
<td>60</td>
<td>$100 \times 10^{-12}$</td>
</tr>
<tr>
<td>Case III</td>
<td>120</td>
<td>$250 \times 10^{-12}$</td>
</tr>
<tr>
<td>HER kinetics</td>
<td>30</td>
<td>$1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Table 2. Electrochemical parameters for the modeling results shown in Fig. 3B

| Case I        | 40                     | $5 \times 10^{-12}$               |
| Case II       | 60                     | $100 \times 10^{-12}$             |
| Case III      | 120                    | $250 \times 10^{-12}$             |
| HER kinetics  | 30                     | $1 \times 10^{-2}$               |
At this point, the system is highly sensitive to increases in $R_{oc}$, which shift the system to higher operating voltages and a region of rapidly decreasing PV-device currents (higher voltages than the solid red circle in Fig. 2B). However, once the operating point shifts to the four-cell curve (at about 15 $\Omega$-cm$^2$), $R_{oc}$ has very little impact on SFE until it reaches ~60 $\Omega$-cm$^2$ (traversing from the * to the open red circle in Fig. 2B or Fig. 3B). In general, for a solar cell with voltage $V_{oc}$ at the maximum power point, the SFE will be relatively invariant to increases in $R_{oc}$ of approximately $\Delta R = V_{oc}/J_{sc}$. The cell modeled here exhibits $V_{oc} = 528$ mV and $J_{sc} \sim 10 \text{ mA cm}^{-2}$, yielding $\Delta R = 50 \Omega$-cm$^2$ and good agreement with the width of the SFE “plateaus” in Fig. 3B. This effect is more pronounced for cells with higher operating voltages, as is evident in Fig. S3.

**Practical Implications.** PV-EC systems such as the artificial leaf pose challenging integration issues beyond those related to the photovoltaic and electrochemical processes alone. In particular if the PV-EC design is wireless, and the entire PV device is immersed in the electrolyte, nontrivial materials challenges must be met to ensure device stability in the vicinity of highly oxidizing conditions (5, 27). Thus, predicting device performance without performing the integration saves substantial research effort.

Consideration of Fig. 1A, as well as the discussion of Figs. 1C and 2B, makes clear that such predictions are possible if the current–voltage properties of the isolated PV and EC systems are known. As discussed, a PV-EC system coupled via direct electrical connection operates under the constraint that $J_{pv} = J_{ec}$ and $V_{pv} = V_{ec}$, a condition that can be found graphically as the intersection of the current–voltage properties. Provided that these properties are known for the PV and EC systems, it is straightforward to identify this operational point.

As a case study, we analyze the OER half-reaction in an experiment nearly identical to that described previously (31). In this experiment, the positive terminal of a Si solar cell is functionalized with the CoB$^-$ catalyst; the Si surface is protected by a terminal of the HER, and replacing the thermodynamic potential with the Nernstian potential for the OER given the solution pH.

In Fig. 4 (Inset), we demonstrate graphically how the illuminated characteristics of this PV-EC system can be found at an applied voltage $V_{app}$. The current–voltage curve of the OER (obtained via steady state Tafel analysis in isolation from the solar cell) is shifted to the lower potentials by the applied voltage; the resulting intersection predicts the behavior of the PV-assisted electrochemical reaction. In Fig. 4, the predicted behavior of the coupled PV-EC system is compared with experiment by using the $J-V$ characteristics of the PV device (not shown for clarity) and the Tafel analysis of the cobalt–borate (CoB$^-$) catalyst (measured in the dark and isolated from the solar cell). The data and the prediction agree to within $<$10 mV. This framework provides insight into interpreting PV-assisted EC reactions. For example, it has been noted that the onset of water oxidation may be reduced by a voltage approximately equal to the solar cell $V_{oc}$ (31). Under the present analysis, we note that the Tafel analysis was performed at current densities at or below 1 mA cm$^{-2}$; inspection of Fig. 4 (Inset) reveals that at such a current density, the system must be coupled near the solar cell’s open-circuit potential and thus a comparable voltage will be used for the electrochemical process.

**Conclusion**

We have outlined a framework for integrating single-absorber solar cells as power sources for electrochemical processes and understanding the efficiency-limiting elements. The steady-state efficiency of coupled PV-EC systems depends on the individual efficiency of each system, but it also depends critically on the efficiency of coupling the two systems. When coupling the two systems directly, by performing each half-reaction on a terminal of the PV device, the coupling efficiency can be modeled using a steady-state equivalent circuit. Additionally, the efficiency of the coupled PV-EC system can be determined given the behavior of each subsystem. We validate this model by correctly predicting the $J-V$ characteristics of a PV-assisted OER to within $<$10 mV. A key result of our analysis is that even when using commercially available Si solar cells, SFE over 15% is achievable provided the design yields very low solution resistance. We have proposed strategies for meeting this challenge.

**Experimental Procedures**

Sample fabrication and experimental procedures for collecting the data in Fig. 4 have been described in detail (31). We provide a summary and describe any differences here. Crystalline Si solar cells were improved relative to the procedures of ref. 31 by including a Si$_3$N$_4$ antireflection layer (75 nm thick, deposited by low-pressure chemical vapor deposition) atop the emitter surface and by optimizing the emitter contact pattern, using photolithography to reduce resistive losses and shadowing. These design changes improved $J_{sc}$ from 27 mA cm$^{-2}$ to 34 mA cm$^{-2}$ and increased the FF from 0.47 to 0.77; consequently, the efficiency improved from 7 to 13%. A 100-nm Ni passivation layer (used in place of indium tin oxide because it functions comparably and facilitates soldering wires to the cell) was deposited by dc sputtering as part of an extensive exploration of catalysts and passivations layers (33). Following Ni deposition, the cobalt–borate (CoB$^-$) catalyst was deposited. Bulk electrolysis was performed in a two-compartment electrochemical cell with a glass frit junction of fine porosity. For the electrodeposition, the working compartment was charged with ~50 mL of solution (25 mL of 0.2 M KB, electrolyte and 25 mL of 1m M Co$^{2+}$ solution). The auxiliary compartment was charged with ~50 mL of 0.1 M KB, electrolyte. The working electrode was the Ni-coated surface of a 1.5 $\times$ 2-cm$^2$ piece of the Si solar cell. Typically, a 1-cm$^2$ area of the working electrode was immersed in the solution and electrolysis was carried out at 0.85 V vs. NHE until 26 mC cm$^{-2}$ of charge passed.

Photoelectrochemistry experiments were performed in a one-compartment quartz cell. The light source was a Sol 2A solar simulator (Newport). The Tafel behavior of surface-passivated, catalyst-functionalized solar cells was measured in the region of water oxidation over a 200-mV range in 10- to 30-mV increments. The measurements were conducted in a solution containing 0.5 M KB, and 1.5 M KNO$_3$ at pH 9.2, using an Ag/AgCl reference electrode and a Pt auxiliary electrode.
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