

Beating the Efficiency of PV-Electrolysis with Tandem Cell Photoelectrolysis

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Solar water splitting is a promising route for hydrogen production from renewable sources: water and sunlight. The hydrogen can be stored and converted to power on demand by means of fuel cells, used as a clean fuel to refuel electric vehicles, or serve as a feedstock for the production of valuable chemicals such as ammonia (via the Haber–Bosch process) or drop-in liquid fuels (by CO₂ hydrogenation). Solar water splitting can be readily achieved by combining two commercial technologies: photovoltaics (PV) and electrolysis. Such combinations have been demonstrated and tested in self-sufficient solar houses,¹ solar hydrogen pilot plants,² solar hydrogen refueling stations,³ and PV solar power plants.⁴ Unfortunately, PV-powered electrolysis (PV-electrolysis for short) is too expensive for large-scale solar hydrogen production.^{5,6} This motivates research on photoelectrochemical (PEC) cells that convert solar energy directly to hydrogen fuel by water photoelectrolysis, thereby combining the functions of light harvesting and electrolysis together. Unlike separate PV-electrolysis systems that have already been demonstrated and tested in several pilot plants,¹⁻⁴ PEC water splitting is still under development and research in this area is academic, for the most part, dealing mostly with lab tests of small-size components and prototype devices.

Therefore, it is too early to predict whether PEC water splitting will beat PV-electrolysis in the commercial playground. Recent technoeconomic analyses suggest that PEC water splitting might become cost-competitive if efficiency and lifetime could be improved significantly compared to present reports on PEC cells.^{5,6} However, some of the underlying assumptions are quite speculative, and unforeseen challenges might get in the way on scaling $< 1 \text{ cm}^2$ prototype devices to $> 10,000 \text{ m}^2$ solar fields. On the bright side, new advances in PEC materials, device architectures and operation schemes, such as the power management and light management schemes presented in this Viewpoint, may render PEC water splitting more competitive than the current scenarios. PEC water splitting is an evolving research field and therefore it is difficult to make reliable predictions for large-scale solar water splitting plants based on current knowledge and experience. As a result, much uncertainty still remains as for the prospects of PEC water splitting to be cheaper than PV-electrolysis. While cost predictions are quite speculative, efficiency is a tangible parameter that has a profound impact on the economy of solar energy technologies. This Viewpoint addresses the efficiency of solar water splitting systems, proposing power management and light management schemes that enable boosting the efficiency of PV-PEC tandem cells with minimal changes in system components, and therefore with minimal add-on costs. Thus, the proposed schemes are expected to improve the competitiveness of PV-PEC tandem cells for solar water splitting.

Due to the relatively high voltage (typically $\geq 1.8 \text{ V}$) that must be applied to drive the overall water splitting reaction, and the need for optimal band edge positions that straddle the potentials of the hydrogen and oxygen evolution reactions, no single photoabsorber material – except for wide bandgap semiconductors that absorb very little sunlight – is able to split water all alone. Therefore, solar-powered PEC water splitting devices are comprised of multijunction PV cells or PV modules

with two or three cells connected in series, in order to provide the necessary bias voltage.⁷ The PV cells (or modules) are often coupled to electrocatalysts for water oxidation and reduction in order to construct integrated PV-electrolysis devices,⁸ aka *artificial leaves*.⁹ Alternatively, they can be coupled to PEC cells comprising a photoelectrode for water oxidation or reduction (photoanode or photocathode, respectively) and a counter electrode for the counter reaction.^{7,10} This configuration yields PV-biased photoelectrolysis (PV-photoelectrolysis for short) devices. According to the taxonomy suggested by Nielander et al.,¹¹ the former configuration belongs to the family of *PV-biased electrosynthetic cells* whereas the latter one belongs to the family of *PV-biased photoelectrosynthetic cells*. Both configurations are often referred to as PEC cells, despite the fundamental differences between them. To avoid confusion, we distinguish between the following configurations of PV-assisted solar water splitting systems and devices: (1) separate PV-electrolysis systems; (2) integrated PV-electrolysis cells (including both wired cells and wireless monolithic cells); and (3) PV-photoelectrolysis cells. These configurations are illustrated in Figure 1. In both the first and second configurations the light harvesting and electrolysis processes are decoupled from each other, and the only coupling between the PV and electrolysis components is electrical. The electrolysis cell serves as the load for the PV cell, therefore the current-voltage (I - V) characteristics of the two cells must be optimally matched for maximum performance.¹² Toward this end, the I - V curve of the electrolysis cell should cross the I - V curve of the PV cell (or module) at the maximum power point (MPP), otherwise the PV cell (or module) would produce less power than it could for an optimally-matched load, thereby giving rise to deleterious coupling loss that dissipates as excess heat. Besides the coupling loss, the power conversion efficiency (PCE) of the PV cell is degraded by intrinsic losses in the electrolysis cell that include voltage (aka overpotential) and current (aka Faradaic) losses. Therefore, the efficiency of PV-electrolysis

systems, both separate as well as integrated ones, is lower than those of the PV cells that drive them. The most significant loss in well-constructed PV-electrolysis systems is the voltage loss that arises from the ubiquitous overpotentials for driving the water oxidation and reduction reactions,¹³ which sum up to ≥ 0.5 V for driving both reactions. This leads to a voltage loss of $\geq 29\%$ with respect to the reversible voltage of water electrolysis. Additional overpotential losses arise from internal resistance (aka Ohmic) losses in the electrolyte and at the membrane that separates the reaction products, i.e., H₂ and O₂ gases. As a result, the solar to hydrogen (STH) conversion efficiency of PV-electrolysis systems is lower by $\geq 30\%$ relative to the PCE of the PV cells that drive them. With a PCE of 20%, which is a typical value for state-of-the-art Si PV panels, this leads to a STH efficiency of 14%.

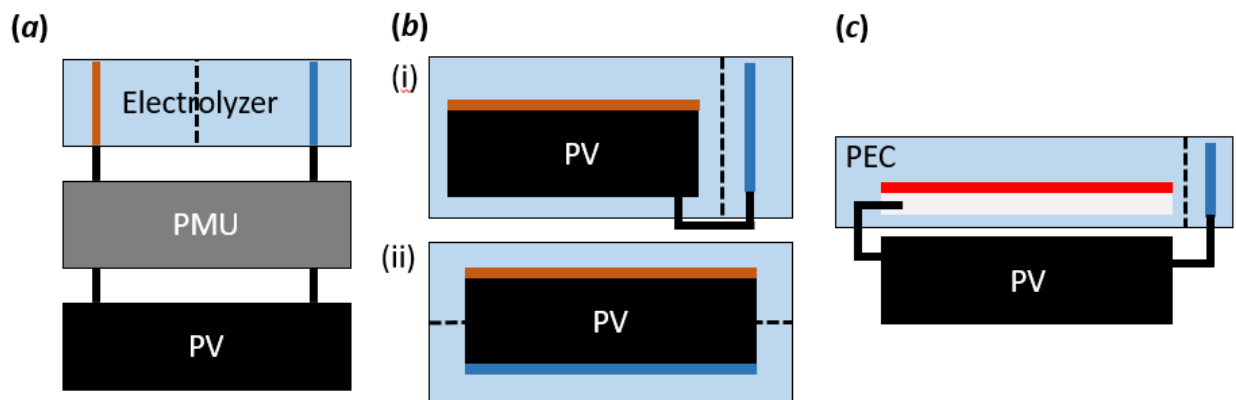


Figure 1. Schematic illustration of PV-assisted solar water splitting configurations. **(a)** Separate PV-electrolysis system, with a PV module coupled to an electrolyzer via a power management unit (PMU). **(b)** Integrated PV-electrolysis cells featuring wired and wireless configurations ((i) and (ii), respectively). **(c)** PV-photoelectrolysis system featuring a PV-PEC tandem cell, with the PEC cell in front of the PV cell. The orange and blue thick lines represent electrodes for oxygen and hydrogen evolution whereas the red thick line in **(c)** represents a photoanode for water photo-oxidation. The dashed black line represents the membrane that separates the O₂ and H₂ gases.

The STH efficiency can be readily boosted by using multijunction PV cells with exceptionally high PCE, such as (In,Ga)P/GaAs/(In,Ga)As or (Ga,In)P/GaAs cells.¹⁴ This route has been pursued by some researchers and there are several reports on PV-electrolysis systems with STH efficiencies exceeding 14%.¹⁵ However, these exceptional results were achieved using multijunction PV cells that are far more expensive than conventional PV cells. Due to their high cost, such cells are employed in niche applications and are unlikely to replace conventional PV cells in large scale applications. Therefore, it is questionable whether this route advances the solar water splitting field any closer to large scale deployment. Thus, instead of using the STH efficiency as the primary benchmark for evaluating PV-assisted solar water splitting systems,¹⁶ we propose another figure of merit (FOM) that considers the ratio between the STH efficiency (η_{STH}) of the entire system and the PCE of the PV module (η_{PV}) that drives the system,

$$FOM = \frac{\eta_{STH}}{\eta_{PV}}. \quad (1)$$

The key advantage of the proposed FOM is that it takes into account the STH efficiency in a normalized fashion, removing trivial boosts that can be readily achieved by means of multijunction PV cells of exceptionally high PCE, but also high cost.

Since the light harvesting and electrolysis processes are decoupled from each other, the STH efficiency of PV-electrolysis systems, separate or integrated ones, is given by the product of the efficiencies of the individual components (i.e., the PV and electrolysis cells) and the coupling efficiency,¹⁷

$$\eta_{STH|PV-electrolysis} = \eta_{PV} \times \eta_{electrolysis} \times \eta_{coupling}. \quad (2)$$

Thus, the FOM for PV-electrolysis systems is

$$FOM|_{PV-electrolysis} = \eta_{electrolysis} \times \eta_{coupling}. \quad (3)$$

Coupling efficiencies approaching 100% can be achieved in well-constructed PV-electrolysis systems,¹⁷ for which the FOM is limited by the electrolysis efficiency. The efficiency of commercial electrolyzers reaches up to 82.3% based on the higher heating value of hydrogen.¹⁸ It is noteworthy that the STH efficiency of PEC water splitting cells is reported based on the free energy of the reaction ($V_{rev}^0 = 1.2291$ V at 25°C),¹⁶ whereas the electrolyzer efficiency is reported based on the higher heating value of hydrogen ($V_{HHV}^0 = 1.4812$ V at 25°C).^{18,19} In this Viewpoint we adhere to the former convention, therefore the highest electrolysis efficiency reported in Ref. 18 becomes 68.3% based on the free energy metrics. Thus, the FOM of PV-electrolysis systems does not exceed 68.3% for the best commercial electrolyzers. It is unlikely that this value would be surpassed by integrated PV-electrolysis systems, for which there are fewer degrees of freedom to optimize performance than in separate systems. Therefore, we take this value (68.3%) as the upper limit for PV-electrolysis systems, separate or integrated ones. The salient question addressed in this Viewpoint is whether this value can be surpassed, and how.

Unlike PV-electrolysis systems in which the light harvesting and electrolysis processes are decoupled from each other, PEC cells with semiconductor photoelectrodes combine both processes together via photoelectrolysis.¹¹ This synergy opens up an opportunity to surpass the efficiency of PV-electrolysis. As mentioned above, most photoelectrodes cannot split water all alone, and therefore they are connected in series with PV cells that provide the additional bias to split water. Thus, the voltage produced at the photoelectrode adds up with the voltage produced at the PV cell, and together they provide the necessary voltage to split water. As a result, the PV cell provides a

smaller voltage than in PV-electrolysis, and therefore more current can be drawn from it. One of the most promising PV-photoelectrolysis configurations that benefits from the synergy between the PV and PEC cells is the tandem cell configuration wherein one of the cells (typically the PEC cell) is in front of the other cell (typically the PV cell), as illustrated in Figure 1(c). Tandem cells separate the sunlight spectrum into two spectral ranges, wherein the high-energy (short wavelength) range is absorbed in the front cell and the low-energy (long wavelength) section is absorbed in the back cell. This enables more efficient light harvesting than in single absorber solar cells, similarly to other tandem solar cells such as multijunction PV cells.²⁰ However, in order to take advantage of the synergy between the PV and PEC cells, and benefit from the possibility to enhance the light harvesting efficiency, the electrical and optical coupling between the front and back cells must be carefully optimized. For tandem cells connected in series, the overall voltage is the sum of the voltages of the individual cells, whereas the current is limited by the smallest current of the cells.²⁰ The back cells receive less light and produce smaller photocurrent than they otherwise could if they were not partially blocked by the cells in front of them. Thus, in order to benefit from this construction, the gain in voltage must be larger than the loss in current. Therefore, tandem cells must be carefully optimized, paying careful consideration to the power and light management of the individual cells, as well as the coupling between them. In the remaining parts of this Viewpoint we examine these considerations and discuss possibilities to optimize the efficiency of PV-PEC tandem cells by employing power management and light management schemes.

Taking Si PV cells coupled to hematite photoanodes as an exemplary case study, Figure 2(a) shows current density – voltage (J - V) curves of a monocrystalline Si PV cell (black solid line curve)²¹ and one of the best thick film hematite photoanode reported to date (red solid line curve).²² For the

latter, we approximate the two-electrode J - V curve of the PEC cell by the three-electrode photocurrent density – potential curve of the photoanode (as reported in Figure 1 of Ref. 23). This approximation neglects the overpotential of the cathode, the Ohmic loss of the electrolyte and other losses in the PEC cell. However, these losses are rather small and therefore they may be neglected. In our tandem cell configuration the PEC cell is in front of the PV cell, as illustrated in Figure 1(c). As a result, the PV cell receives less light and consequently it produces a smaller short-circuit photocurrent (J_{sc}) than it would without the PEC cell in front of it. Thick film hematite photoanodes absorb all of the light at wavelengths shorter than 590 nm, thereby reducing the J_{sc} of the Si PV cell by approximately 30%, as confirmed by solar-simulated J_{sc} measurements with and without a thick film hematite photoanode in front of the Si PV cell. Besides the reduction in J_{sc} , the voltage produced by the PV cell is also reduced, but the voltage loss is much smaller than the current loss because of the logarithmic dependence of the voltage on the current. The J - V curve of the back PV cell was calculated from the J - V curve of the pristine PV cell without the PEC cell in front of it using the ideal diode equation,²³

$$J = J_{sc} - J_0 \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]. \quad (4)$$

For the hematite PEC / Si PV tandem cell considered here as a case study, the J - V curve of the back PV cell was calculated by reducing 30% of the J_{sc} of the pristine PV cell without the PEC cell in front of it. The resultant J - V curve is shown by the black dashed line curve in Figure 2(a).

(a)

(b)

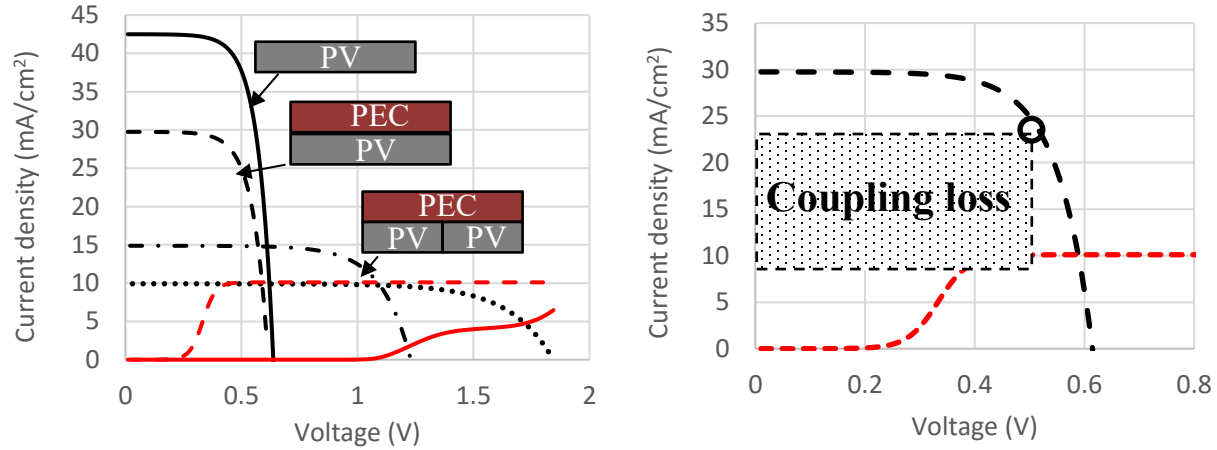


Figure 2. (a) Current density – voltage (J - V) curves of a monocrystalline Si PV cell (black solid line curve),²¹ and one of the best thick film hematite photoanodes reported to date (red solid line curve).²² The dashed, dotted-dashed and dotted black curves present calculated J - V curves for one, two and three series connected PV cells after subtracting 30% of the short-circuit photocurrent due to light absorption in the front PEC cell. The red dashed line curve presents a hypothetical J - V curve of an ideal PEC cell. (b) Re-plotting the J - V curves from (a) for the Si PV back cell and an ideal PEC front cell (black and red dashed line curves, respectively). The black circle marks the MPP of the PV cell, and the dotted rectangle represents the coupling loss that arises from non-optimal coupling of the PV and PEC cells for which the operation point (where the two curves cross each other) is far away from the MPP of the PV cell.

In the tandem cell configuration considered here the front and back cells overlap each other, therefore their areas are the same. Thus, the J - V curves in Figure 2 represent the area-normalized J - V curves of the respective cells, so the operation point of the tandem cell is where the J - V curves of the PV and PEC cells cross each other. As can be seen in Figure 2(a), the J - V curve of the single PV cell does not cross the J - V curve of the PEC cell, meaning that the voltage produced by the PV cell is insufficient to drive the water splitting reaction in this PEC cell. To overcome this

shortcoming, two or three PV cells can be connected in series, thereby doubling or tripling the voltage, respectively, while reducing the current density by the same factor. This is shown by the black dashed-dotted and dotted line curves presenting the predicted J - V curves of two or three series connected PV cells, respectively, partially blocked by the PEC cell in front of them. The J - V curves of the PV module with three PV cells connected in series (black dotted line curve) and of the hematite photoanode (red solid line curve) cross each other at a current density of 4.9 mA/cm², which corresponds to a STH efficiency of 6%. This value is less than a half of the STH efficiency that can be achieved by connecting the same PV cell, with a maximum PCE of 18.8%, to an electrolyzer with an efficiency of 68.3%, yielding a STH efficiency of 12.8%. This is not surprising considering that hematite photoanodes are still far away from reaching their full potential performance. To assess the potential of high-performance photoelectrodes that may become available in the future, we hypothesize an ideal PEC cell displaying a hypothetical J - V curve as shown by the red dashed line curve in Figure 2(a). Such a PEC cell could be driven by a single PV cell, yielding a current density of 10.1 mA/cm², which corresponds to a STH efficiency of 12.4%. This would be a remarkable result, but it is still lower than the STH efficiency that can be achieved by connecting the same PV cell to an electrolyzer. So the salient question is whether there is something else that can be done to improve the efficiency of PV-PEC tandem cells and make them more competitive so they could possibly beat PV-electrolysis.

In order to answer this question, let us examine more closely the J - V curves of the ideal PEC cell and the partially blocked Si PV cell from Figure 2(a), which are replotted in Figure 2(b) without the other curves. The J - V curves cross each other at 0.6 V, far away from the MPP of the partially blocked PV cell at 0.5 V (marked by the black circle in Figure 2(b)). This means that the PV cell operates sub-optimally, losing a lot of potentially useful power that the PV cell would be otherwise

capable of generating (marked by the dotted rectangle in Figure 2(b)). This loss of potential power generation capacity is referred to as the coupling loss.¹² It dissipates as excess heat, which would likely need to be removed to maintain the performance of the cell. In the hypothetical case study featured in Figure 2(b) the coupling loss amounts to 7.8 mW/cm^2 , that is 42% of the maximum power that can be achieved by the PV cell. This loss can be recuperated by introducing a simple modification in the electrical circuit. Instead of connecting the PV cell in series to the PEC cell alone, another load (representing some useful power consumption, see below) can be added in parallel to the PEC cell, as illustrated in the inset of Figure 3(a). The parallel load reduces the combined resistance of the overall load connected to the PV cell, thus enabling the overall load resistance to be matched to the MPP of the PV cell. The influence of the parallel load on the predicted J - V curves is shown in Figure 3(a). The blue line represents the resistance of the parallel load whereas the red solid line curve is the combined resistance of the overall load comprising the PEC cell and the parallel load. The black and red dashed line curves are replotted from Figure 2(a). With the parallel load resistance in place, the tandem cell can be readily tuned to operate at the MPP of the PV cell, thereby recuperating the coupling loss that existed without it and minimizing excess heat generation.

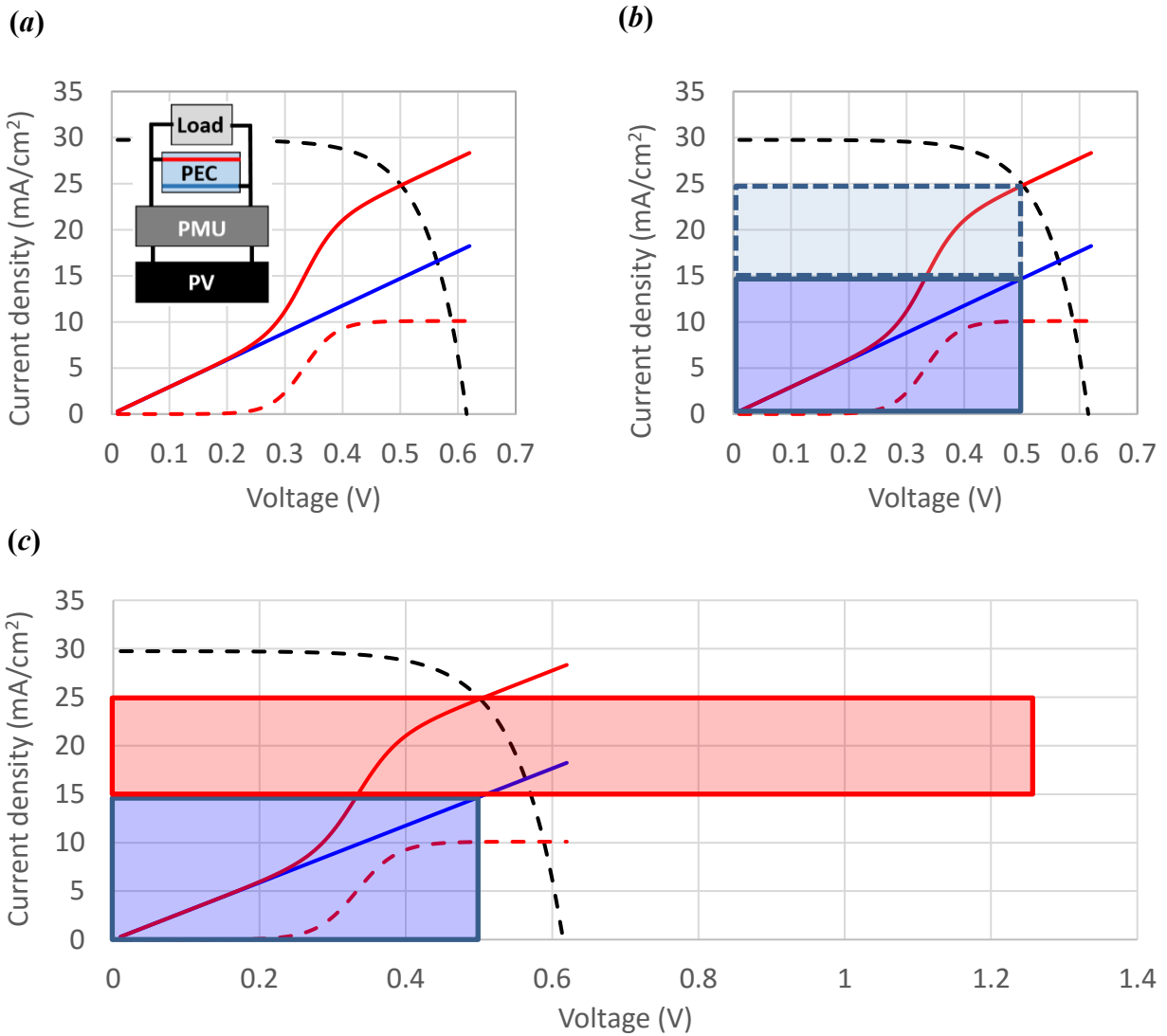


Figure 3. (a) Predicted J - V curves (taken from Figure 2) of a hypothetical tandem cell comprising an ideal PEC cell in front of a monocrystalline Si PV cell (red and black dashed line curves, respectively). The blue line represents the resistance of an auxiliary load connected in parallel to the PEC cell, as illustrated in the inset. The combined J - V characteristics of the overall load connected to the PV cell is presented by the red solid line curve. (b) Replotting the J - V curves from (a) and showing the net electrical power produced by the cell and the electrical power that drives the PEC cell (dark and pale blue rectangles, respectively). (c) Replotting the J - V curves from (a) and showing the net electrical power and chemical power produced by the tandem cell (blue and red rectangles, respectively).

The proposed system produces both electrical and chemical power. The chemical power production corresponds to hydrogen that can be stored in cylinders or other vessels, thereby converting solar energy into chemical energy stored in hydrogen bonds. The net electrical power produced by the system can be used to power auxiliary system components such as pumps and cooling systems, stored in batteries, or sold to the grid. The overall electrical power produced by the system is shown by the blue rectangles in Figure 3(b). The darker rectangle corresponds to the net electrical power produced by the cell whereas the pale one corresponds to the power that drives the PEC cell to split water. The chemical power produced by the system is shown by the red rectangle in Figure 3(c), together with the net electrical power (shown by the blue rectangle). Altogether, the system splits water at a current density of 10.1 mA/cm^2 which corresponds to a STH efficiency of 12.4%, and on top of that it also produces a net electrical power density of $14.7 \text{ mA/cm}^2 \times 0.5 \text{ V} = 7.4 \text{ mW/cm}^2$ which corresponds to a net PCE of 7.4%. Thus, the overall efficiency is 19.8%, higher than the PCE of the PV cell that drives the system (18.8%), and considerably higher than the efficiency that can be achieved by PV-electrolysis using the same PV cell. This hypothetical case study demonstrates the potential advantage of co-generation of chemical and electrical power, which is readily achieved by adding another load in parallel to the PEC cell.

Co-generation of chemical and electrical power is possible for wired PV-assisted water splitting devices, but not for wireless monolithic cells such as the one illustrated in Figure 1(b)(ii). Wired device configurations provide more degrees of freedom than wireless configurations, such as the possibility to place a safety switch, another parallel load, and a power management unit (PMU) between the PV cell and electrolysis or photoelectrolysis cell. The safety switch is important for immediate shut down in case of potential fire hazards. The parallel load plays an important role in

matching the current and voltage output of the PV cell to the input characteristics of the load connected to it. Therefore, it should have a tunable resistance in order to respond to changes in the J - V characteristics of the PV cell due to variations in light intensity. The PMU can track the MPP of the PV cell and tailor the current and voltage output to match the combined resistance of the PEC cell and the parallel load. Such devices are employed in separate PV-electrolysis systems,²⁴ and using them in PV-PEC tandem cells is advisable in order to provide the flexibility required to optimize performance. The power loss of well-constructed PMUs can be made very small and therefore it is neglected here. Under this approximation, the current \times voltage product at the output terminals of the PMU is equal to the power produced by the PV cell that drives the system,

$$I_{out} \times V_{out} = P_{PV}. \quad (5)$$

The current is split between the PEC cell and the parallel load,

$$I_{out} = I_{PEC} + I_{load}, \quad (6)$$

and the total useful power produced by the system is,

$$P_{total} = P_{chemical} + P_{electrical} = I_{PEC} \times V_{rev}^0 + I_{load} \times V_{out}. \quad (7)$$

In analogy to equation 1 we define the figure of merit of PV-electrolysis and PV-photoelectrolysis systems that co-generate both chemical and electrical power,

$$FOM = \frac{P_{total}}{P_{PV}}. \quad (8)$$

Figure 4 plots how this FOM depends on the fraction of the total power production that goes towards chemical power generation, $X_{chem} = P_{chem} / P_{total}$ for hypothetical power-managed systems.

The FOM was calculated using equations 5 through 8 for the following scenarios: (i) PV-electrolysis wherein the electrolysis is carried out at a voltage of 1.8 V (which corresponds to an electrolysis efficiency of 68.3%), shown by the black curve; (ii) PV-PEC tandem cells wherein the PEC cells operate at different voltages (0.5, 1.0 or 1.5 V) and current densities (4, 6, 8 and 10 mA/cm²), marked by different colors as indicated in the legend. The calculations were made for a fixed operation point of the PEC cells at the respective voltage and current density values as indicated in the legend. Varying X_{chem} corresponds to varying the current ratio I_{PEC} / I_{out} . This can be done, for instance, by connecting more or less PEC cells to the PV power source, thereby increasing or decreasing X_{chem} , respectively. The same concept applies also for PV-electrolysis systems that co-generate chemical and electrical power in a similar fashion. The solid line curves in Figure 4 correspond to a scenario in which the PV cells in the array are always covered by PEC cells in front of them, regardless of the current drawn by the PEC cells, I_{PEC} . This reduces the PV power production by approximately 30% for hematite PEC / Si PV tandems, as discussed above. It is noteworthy that in this scenario the PV power production is reduced by a fixed amount (30% in this hypothetical case study) even for a situation wherein all the PEC cells in the array are disconnected and the system produces only electrical power. Such a situation might happen, occasionally, when the parallel load (e.g., the grid) requires all of the power produced by the system. The broken line curves in Figure 4 represent another scenario in which the reduction in PV power output scales with the rate of hydrogen production by the PEC cells. Thus, when no hydrogen is produced, the respective PEC cells are removed from the optical path and the respective PV cells receive the full sunlight spectrum. Such flexibility is an advantage of a modular, rather than integrated (i.e., monolithic), system. The filled circles at the right hand side of Figure 4 represent conventional PV-PEC tandem cells that produce only hydrogen and no

electrical power, as illustrated in Figure 1(c). The rate of hydrogen production for these cells corresponds to the current densities indicated by the color code in the legend of Figure 4. The calculations in Figure 4 were done for PV cells with a PCE of 20% at the MPP. The results are presented in terms of the FOM on the y-axis. In order to get the total PCE (combined chemical and electrical power), the FOM values on the y-axis should be multiplied by the PCE of the PV cell (i.e., 20% for this case study).

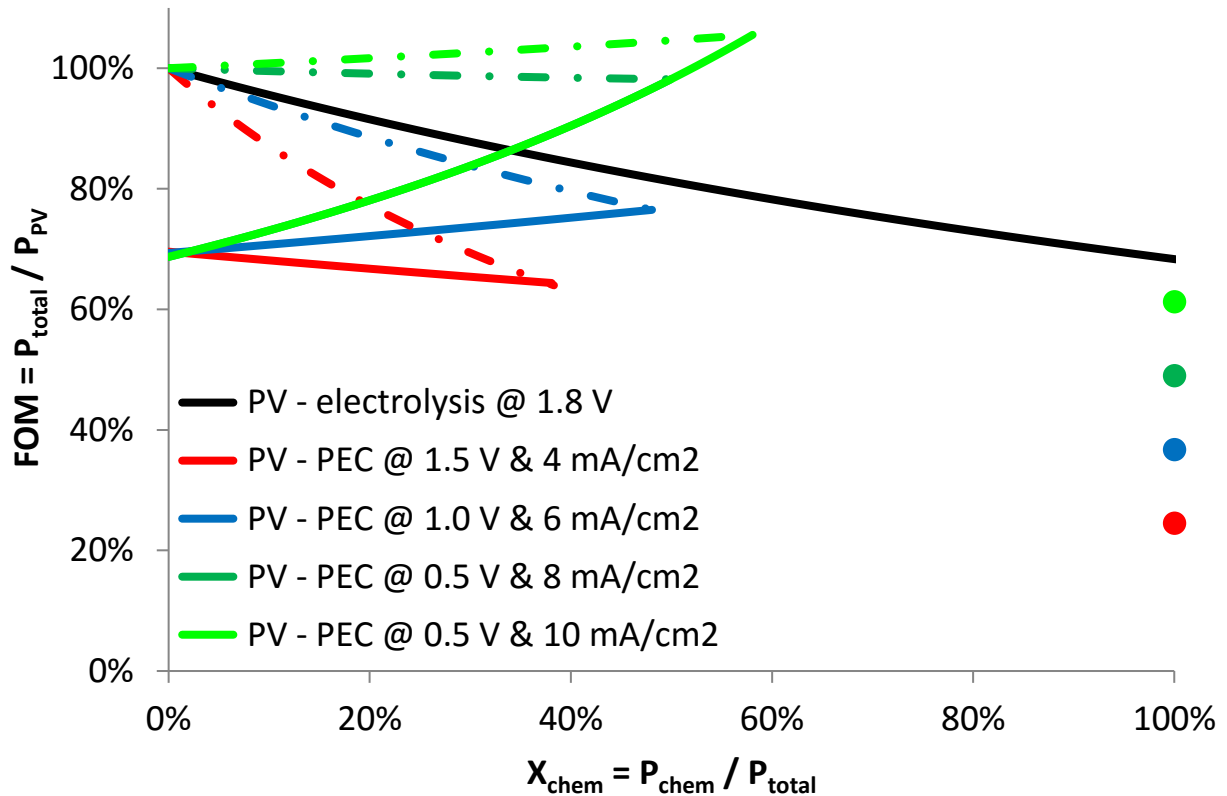


Figure 4. Calculated FOM as a function of the fraction of the total power production that goes towards chemical power generation, $X_{chem} = P_{chem} / P_{total}$, for hypothetical PV-electrolysis (black curve) and PV-PEC tandem cells (color curves) that co-generate both chemical (i.e., hydrogen) and electrical power. The calculations assume PV cells with a PCE of 20%, electrolysis efficiency

of 68.3% for the electrolyzers, and PEC cells operating at the bias voltages and current densities as indicated by the color code in the legend. Solid lines represent a scenario in which all the PV cells in the array are always covered by PEC cells in front of them that reduce 30% of their power, due to light absorption in the PEC cells. Broken lines represent another scenario wherein the reduction in PV power production scales with the chemical power production by the PEC cells. The filled circles on the right hand side of the figure represent conventional PV-PEC tandem cells that produce only hydrogen and no electrical power. Their colors correspond to their respective current densities, as indicated in the legend.

Figure 4 demonstrates the advantage of using the proposed power management scheme. Splitting the PV current output between the PEC cell and another parallel load enables optimal operation of the PV cell at the MPP, regardless of the current drawn to the PEC cell. Excess current that is not drawn to the PEC cell produces electrical power that can be used to power auxiliary system components such as pumps and cooling systems, stored in batteries, or sold to the grid. As described above, without the parallel resistance, the PV cell does not operate at the MPP, giving rise to a power loss (that is the coupling loss marked by the dotted triangle in Figure 2(b)) that dissipates as excess heat that should be removed in order to avoid overheating of the PV cell. All in all, the total available power production (including both hydrogen and electrical power production) exceeds the chemical power production of conventional PV-PEC tandem cells comprising of the same PV and PEC cells, shown by the filled circles on the right hand side of Figure 4. If the PEC cell displays a flat photocurrent plateau at the selected operation voltage (V_{out}), as in our hypothetical case study (see the red dashed line curve in Figure 2(b)), the PV cell can be operated at its MPP while the chemical power production by the PEC cell remains maximal. In

this case, the electrical power production does not come at the expense of hydrogen generation, and the STH efficiency remains the same with or without the additional parallel load. This is a win-win situation that enables boosting the total power production while minimizing excess heat generation, without any penalty. Besides surpassing the efficiency of conventional PV-PEC tandem cells, the proposed power management scheme also provides a viable route to surpass the efficiency of PV-electrolysis systems. In the hypothetical case study presented in Figure 4, the conventional PV-PEC tandem cells fall short of PV-electrolysis even for an ideal PEC cell that produces a photocurrent of 10 mA/cm^2 at a bias of only 0.5 V, which is very generous for the PEC cells reported to date. Without this power management scheme, such a PEC cell could reach a STH efficiency of 12.3% when coupled to a suitable PV cell that provides the necessary bias to drive the PEC cell. This would be a remarkable result for a PV-PEC tandem cell, but nevertheless it falls short of the STH efficiency that can be achieved by connecting the same PV cell (with a PCE of 20%) to an electrolyzer (with an efficiency of 68.3%) which yields a STH efficiency of 13.7%. Our approach enables reaching a total PCE of 21%, as shown by the pale green curve in Figure 4 that reaches a maximum FOM of 105.5%. This value exceeds the total PCE of PV-electrolysis systems producing the same amount of hydrogen. Noteworthy, it also exceeds the electrical PCE of the PV cell that drives the system (20%). This is due to the enhanced light harvesting efficiency of tandem solar cells.²⁰ However, in order to surpass the PV-electrolysis efficiency the PEC cells should operate at a low bias voltage, smaller than 1 V for the hypothetical case study featured in Figure 4. The calculations presented in Figure 4 assume hypothetical tandem cells in which the power produced by the PV cells is reduced by 30% due to light absorption in the PEC cells in front of them. This is a good approximation for Si PV cells in tandem with photoelectrodes with a bandgap energy of 2.1 eV such as hematite or cuprous oxide. Similar calculations can be carried

out for other material combinations, as well as for PV-PEC tandem cells with multijunction PV cells. An in-depth analysis of the optimal material combinations is beyond the scope of this Viewpoint. However, the underlying considerations are similar to tandem solar cells, as discussed elsewhere.²⁰

Besides boosting the efficiency and minimizing wasted heat production, the proposed power management scheme also provides flexibility in electrical and chemical power production. When the need for electrical power is high the PEC cells can be disconnected from the PV power source for maximal electrical power production, and when the need for electrical power is low, they can be connected to produce storable chemical energy. This flexibility is important for load leveling and storage of intermittent solar power, one of the greatest challenges in solar energy conversion. In order to make the most out of this flexibility we propose an active light management scheme that activates the respective PEC cells when desired (driving them to the ON state), and deactivates them when they are not needed (driving them to the OFF state) with minimal power loss in the OFF state. An elegant way of switching between the ON and OFF states with minimal efforts is illustrated in Figure 5.²⁵ The PEC cell is comprised of an array of double-sided photoelectrodes that can be tilted into or out of the optical path, similarly to Venetian blinds, thereby activating or deactivating the PEC cells upon demand. It is noteworthy that the Venetian blind design is compatible with the resonant light trapping approach proposed by us several years ago in order to boost the efficiency of ultrathin film hematite photoanodes.²⁶ Active light management schemes such as this one enable switching the respective cells from full electrical power production to combined electrical and chemical power co-production while minimizing the PV power loss in the OFF state, thereby tracking the broken line curves rather than the solid line curves in Figure 4.

This enhances the overall PCE, except for the case of maximal chemical power production for which the efficiency becomes the same in both cases (see Figure 4).

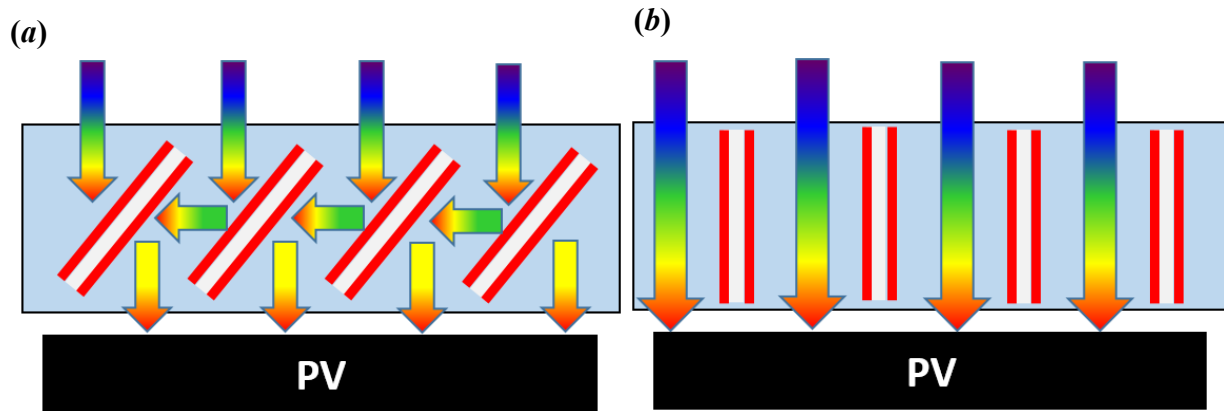


Figure 5. Schematic illustration of the Venetian blind concept for active light management between the front PEC cell and back PV cell. **(a)** ON state. **(b)** OFF state.

In summary, this Viewpoint presents power management and light management schemes designed to boost the efficiency of PV-PEC tandem cells by minimizing the coupling loss that arises from operating the PV cell far away from its MPP. In essence, the proposed power management scheme adds another load in parallel to the PEC cell. This load represents auxiliary system components such as pumps and cooling systems, or the electrical grid, thereby turning the coupling loss that generates deleterious excess heat into useful electrical power. Co-production of electrical power and storable chemical power provides an elegant solution for load leveling of intermittent solar power. To fully benefit from the flexibility to tune chemical and electrical power production on demand, we propose an active light management scheme that activates the respective PEC cells in the array when desired and minimizes the PV power loss when they are deactivated. Our approach enables boosting the efficiency of PV-PEC tandem cells well above the efficiency of conventional tandem cells comprising the same materials. Moreover, it enables the efficiency of PV-PEC

tandems to surpass that of PV-electrolysis systems. Toward this end, the voltage gain due to the photovoltage generated in the PEC cell²⁷ must be larger than the current loss induced by the PEC cell.

ASSOCIATED CONTENT

N/A

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Notes

The authors declare no competing financial interest.

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