Hydrogen from Sunlight and Water: A Side-by-Side Comparison between Photoelectrochemical and Solar Thermochemical Water-Splitting

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ABSTRACT: Photoelectrochemical (PEC) and solar thermochemical (STCH) water-splitting represent two promising pathways for direct solar hydrogen generation. PEC water-splitting integrates multiple functional materials and utilizes energetic electrons and holes generated from sunlight to produce hydrogen and oxygen in two half-reactions, while STCH water-splitting couples a series of consecutive chemical reactions and uses absorbed heat from sunlight to generate hydrogen and oxygen in two full reactions. In this Focus Review, the basic operating principles, sunlight utilization, device architecture, reactor design, instantaneous and annually averaged solar-to-hydrogen (STH) conversion efficiency, and the operating conditions and constraints of both pathways are compared. A side-by-side comparison addresses some common sources of confusion and misinterpretation, especially in the evaluation of STH conversion efficiencies, and reveals distinct features and challenges in both PEC and STCH technologies. This Focus Review also addresses materials and device challenges in PEC and STCH for cost-competitive hydrogen generation.

Technologies for large-scale, long-term energy storage that can accommodate weekly and seasonally variable energy needs are expected to play a critical role in a future of significantly expanded renewable energy use. Cost-competitive “green” hydrogen from sunlight could find uses in multiple industrial sectors including transportation, chemical synthesis, iron and steel production, fertilizer synthesis, and in biorefineries. Green hydrogen has the potential to meet long-term, terawatt scale energy storage demands.1 Water-splitting via solar thermochemical hydrogen (STCH) and photoelectrochemical (PEC) are two important approaches for sunlight-driven “green” hydrogen generation currently being explored by the research and development community. While both technologies use the same feedstock, i.e., sunlight and water, and have a common end product, i.e., hydrogen, the two technologies have rarely been compared and contrasted due to the significant differences in materials, fundamental principles, and operating conditions. Recent DOE-supported benchmarking efforts in the HydroGEN consortium brought multiple technological pathways for advanced water-splitting together to establish and maintain a balanced portfolio of documented “best practices” among four classes of technologies, namely low- and high-temperature electrolysis (LTE and HTE, respectively), PEC, and STCH.2,3 Recent techno-economic analysis (TEA) of both PEC and STCH water-splitting approaches showed promise for achieving low cost hydrogen using renewable energy inputs. For PEC, various types of PEC devices with forward-looking materials properties and cost estimate yielded levelized cost of H₂ at plant gate at <US$2/kg.4,5 For STCH, the current estimated H₂ cost is still high (US$4−6/kg),6 and the solar field and the tower have the highest contribution to this cost. Pathways to achieve a cost target of US$2/kg have been presented in the literature.7 In this Focus Review, we will first briefly describe the operating principles of the two approaches for direct solar hydrogen generation, PEC and STCH, and their device or reactor embodiment, and then we will compare these two side-by-side in terms of sunlight utilization, anticipated solar-to-hydrogen conversion efficiency, and operating conditions. In addition, we include a discussion of materials and system challenges for each technology. This Focus Review aims to compare the unique aspects and challenges for PEC and STCH, to lay the

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groundwork for long-term development of solar fuel technologies. Importantly, we do not aim to make an argument that one approach is better than the other, as both show distinct promise and advantages as well as challenges.

## GENERAL OPERATING PRINCIPLES OF PHOTOELECTROCHEMICAL AND SOLAR THERMOCHEMICAL WATER-SPLITTING

Photoelectrochemical (PEC) water-splitting cells are integrated solar fuels generators incorporating multiple functional materials and they couple PEC processes to produce hydrogen and oxygen from sunlight and water. Figure 1a illustrates key photoelectrochemical processes in a typical device in which the semiconductor materials harvest the incident sunlight, and any materials or components in the optical path between the sun and the semiconductors could potentially modulate and alter the light absorption. The light illumination can be from either side of the cell or both sides depending on the detailed configuration of the system. Typically, three main categories include “photocathode and dark anode”, “photoanode and dark cathode”, and “photocathode and photoanode”. In all three categories, the overall voltage generated by the photoabsorbers has to exceed the required voltage for the water-splitting reaction. Figure 1a used “photocathode and photoanode” as the generic illustration for the PEC system. Absorbed photons in the semiconductor material generate energetic electrons and holes, which are transported to electrocatalysts via bulk and interfacial charge transport processes. Next, electrocatalysts perform water-splitting and simultaneously produce gaseous H₂ and O₂ at the catalytic sites. The equations below indicate the possible two half-reactions and corresponding net reaction involved in the complete process:

**Half-reaction at cathode (reduction):**

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \]  

**Half-reaction at anode (oxidation):**

\[ 2\text{OH}^- + 2\text{h}^+ \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \]  

**Net reaction:** \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \]

**OR**

In addition, ionic transport between the cathode and anode electrolytes and product separation are necessary to maintain efficient and safe operation of the cell. Note that all these processes couple to produce a single rate of reaction for water-splitting in the PEC device. To overcome the thermodynamic potential \( \Delta U_{\text{rxn}} \) between oxygen evolution reaction (OER) at the anode \( (1.23 \text{~V~vs~RHE}, \text{where RHE is the reversible hydrogen electrode potential}) \) and hydrogen evolution reaction (HER) at the cathode \( (0 \text{~V~vs~RHE}) \), the total voltage (Fermi level splitting) of cathode and anode needs to be large enough to sustain the full reaction. In many cases, as shown in Figure 1, the conduction band edge \( (E_{cB}) \) of the cathode and the valence band edge \( (E_{VH}) \) of anode straddle the energy levels for water-splitting reactions, e.g., the HER at 0 V vs RHE and the OER at 1.23 V vs RHE. It is important to note that band edge positions that straddle the energy levels of water-splitting reactions are not required as long as the overall Fermi-level splitting of the photocathode and photoanode exceeds 1.23 V to sustain the full reaction. In other words, a p-type photocathode with the conduction band position lower than 0 V vs RHE can still drive HER upon illumination due to the surface inversion of the p-type semiconductor that effectively unpinned the band edge position. In addition, solid-state, buried junctions using traditional photovoltaic materials, such as Si, GaAs, etc., are often used to circumvent the stringent requirements for the band edge positions and to achieve high-efficiency solar water-splitting performances.

Solar thermochemical (STCh) cycles use sunlight in the form of adsorbed heat to produce hydrogen and oxygen from water. Although water can thermally dissociate just with heat (known as thermolysis), this direct dissociation requires an impractically high operating temperature \( (>2500 \text{~K}) \) to obtain a significant degree \( (>4\%) \) of hydrogen. Furthermore, the separation of the products at high temperatures is challenging. STCh water-splitting reactors circumvent these difficulties by carrying out the dissociation reaction through a series of consecutive chemical reactions, such that O₂ and H₂ are generated in different steps, either separated temporally or spatially. In addition to water as the sole consumed reactant, one or more reactants actively participate in the process without being “net” consumed. Many sequences of reactions have been proposed like volatile metal oxide cycles (e.g., Zn/ ZnO cycle or SnO₂/SnO cycle), phase change stoichiometric oxides (e.g., FeO₂/FeO cycle or metal-substituted ferrites cycles) or multistep cycles (e.g., hybrid sulfur cycle or manganese oxide-based cycle). However, currently two-step redox off-stoichiometric metal oxide (MOₓ) thermochemical cycles garner most of the ongoing research efforts among the thermochemical water-splitting cycles, either with cerium-based oxides or perovskites. The metal oxide cycles involve only two reactions (one per each step) based on a redox swing between...
an oxidized and reduced form of a candidate material, MOₓ, for which the metal ion (M) can assume multiple oxidation states and the oxygen stoichiometry can vary continuously.46,47 eqs 7-9 below summarize the reactions involved in the two-step off-stoichiometric metal oxide cycle:

Reduction: \[ \frac{1}{\delta} \text{MO}_x \rightarrow \frac{1}{\delta} \text{MO}_{x-\delta} + \frac{1}{2} \text{O}_2 \]  
(7)

Oxidation: \[ \frac{1}{\delta} \text{MO}_{x-\delta} + \text{H}_2\text{O} \rightarrow \frac{1}{\delta} \text{MO}_x + \text{H}_2 \]  
(8)

Net reaction: \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]  
(9)

Figure 1b illustrates the overall operating principle of the two reaction steps in STCH water-splitting. The first step involves the reduction reaction, which is highly endothermic and requires a high-temperature energy source for the reaction to occur. Note that the metal-oxide reoxidation reaction enthalpy must be higher than the water-splitting reaction enthalpy at the reoxidation temperature, and tends to range between 250 and 500 kJ/mol of \( \text{H}_2 \). Concentrated solar thermal technologies such as point focus on a solar tower can provide this heat in a cost-effective renewable form through the sunlight reflection from an array of mirrors focused on a concentrated spot into a receiver/reactor, where the active material heats up and the reduction reaction occurs. The second step involves the reoxidation reaction, which is mildly exothermic and is favorable at lower temperatures. Temperature, partial pressure of oxygen, and concentration of gases play a key role in these reactions. The reduction reaction depends sensitively on temperature (\( T_R \)) and partial pressure of oxygen (\( p_{O_2} \)), with the degree of reduction or off-stoichiometry (\( \delta \)) being a strong function of both variables, \( T \) and \( p_{O_2} \). To avoid the reverse reaction, it is necessary to remove the oxygen released from metal oxide from the system prior to cooling in preparation for the reoxidation reaction. The reoxidation reaction highly depends on both temperature (\( T_{O_x} \)) and the amount of excess reactant steam relative to available oxygen ion vacancies. The higher the reoxidation temperature, the larger amount of excess steam, whereas a lower reoxidation temperature requires shedding a large amount of sensible heat after the reduction step and then injecting a similar amount to raise the temperature of the material in preparation for another reduction step.

Unlike solar thermochemical water-splitting, in which two full redox reactions take place, photoelectrochemical water-splitting uses two half-reactions, e.g., hydrogen evolution reaction and oxygen evolution reaction.

While the overall water-splitting reaction is identical for both technologies, the STCH process involves two full reactions, where the two electrons left behind when removing an oxygen atom from the anion lattice nominally moves to the cation lattice within the solid-state \( \text{MO}_x \) material during the reduction reaction. As a result, the reduction reaction and reoxidation reactions in STCH are separated in time (temporally) and/or in space (spatially). Unlike STCH, in which two full redox reactions take place, PEC water-splitting uses two half-reactions, e.g., HER and OER. As a result, the two half-reactions must be performed simultaneously without any temporal separation. While the vast majority of the reported PEC water-splitting system performed HER and OER at the same rate,55-18,46 additional redox couples or charge carriers can be introduced to the PEC device to replace either HER or OER for the spatial and temporal decoupling of hydrogen and oxygen generation.47,48 It is also important to note that the reduction reaction or the oxidation reaction in PEC commonly refers to water reduction (eq 1) or water oxidation (eq 5), respectively. In contrast, for STCH the reduction reaction and the reoxidation reaction refers to the reduction and reoxidation of the redox materials and not of water. As a result, oxidation produces \( \text{O}_2 \) and \( \text{H}_2 \) in a PEC device and STCH reactor, respectively; while reduction produces the reverse, i.e., \( \text{H}_2 \) and \( \text{O}_2 \) in a PEC device and STCH reactor, respectively.

### DEVICE/REACTOR ARCHITECTURE COMPARISON BETWEEN PHOTOELECTROCHEMICAL AND SOLAR THERMOCHEMICAL WATER-SPLITTING

The device architecture and reactor design in both PEC and STCH water-splitting are critical to the overall performance of the system. Two general types of PEC water-splitting device architectures, have been modeled and experimentally demonstrated at the laboratory scale.4,49,50 A Type 1 PEC device indicates a system where the catalyst on a light absorber is configured in the form of particles suspended in the electrolyte, as shown in Figure 2a. Both a single chamber device, where hydrogen and oxygen coevolve, and a dual-chamber device, for which a redox shuttle is required in the Z scheme reaction, have been proposed and studied for particle-based systems. Based upon years of research on particle-based photocatalyst research, a flat panel-like, “catalyst sheet” device using Al doped \( \text{SrTiO}_3 \) was demonstrated in recent years at large solar collection area of \( \sim 1 \) m\(^2\) that coevolved \( \text{H}_2 \) and \( \text{O}_2 \) at the catalyst surface.51 While the Type 1 PEC device architecture has shown great promise in many technoeconomic analyses (TEA), the solar-to-hydrogen (STH) conversion efficiency is currently limited to <2%.52,53 A Type 2 PEC device indicates a system for which catalyst coated planar semiconductor materials and membrane separators are configured to maximize the light absorption and to minimize the transport losses in the device with achievable STH efficiencies of about 20%.13-18 Both PEC architectures can operate under ambient sunlight or relatively low concentration, e.g., a concentration factor \( C < 10 \). However, a recent development with a significantly higher concentration factor \( C \approx 474 \) has also been demonstrated in a PEC system.54

For STCH, there are two conceptual reactor system designs: both reactions are placed in the same reactor or each one is placed in different reactors. In the first configuration (Figure 2c), the metal oxide remains in the same chamber and the reactions take place sequentially, hence temporal separation of \( \text{O}_2 \) and \( \text{H}_2 \). To have quasi-continuous hydrogen production and no to minimal waste of available solar radiation, two (or more) reactors are placed in parallel alternating between oxygen and hydrogen production.59,55,56 For the second configuration (Figure 2d), the metal oxide moves from one reactor to the other and back again to the first. While the reduction reaction takes place in the on-sun reaction chamber, the reoxidation reaction takes place in an off-sun reaction.
chamber. Thus, the production of H₂ is continuous and the separation of O₂ and H₂ is spatial. In addition, this configuration facilitates heat recovery, which is essential to obtain high efficiency. Technologically, the two main solutions proposed for this system concept are the moving bed of particles (or other form factor) and the counter-rotating rings. The moving particle concept has a higher operating flexibility since the particles can be stored and used on demand, being possible to increase the capacity factor of the plant, however, that eliminates some opportunities for solid-solid heat recovery. The counter-rotating ring(s) reactor, on the other hand, simplifies the system by combining both reactors and the heat exchanger into a single device, but strongly couples the two reaction rates, limiting opportunities to independently vary the residence times for each reaction.

In PEC devices, the sunlight collection area is often comparable to the photoelectrochemically active area for the solar-driven water-splitting reaction, with the exception of solar concentrator coupled PEC devices, where the sunlight collection area is larger than the photoelectrodes by the concentration factor in the PEC device. As a result, the light absorber as well as the electrocatalysts for the water-splitting reaction often occupy a large geometric area in the system. For electrocatalysts, both uniformly coated, ultrathin catalyst layers

Figure 2. Schematic illustrations of device architectures for (a) particle-based PEC device, (b) planar catalyst-coated semiconductor PEC device, (c) two fixed-bed alternating reactors STCH system, and (d) moving particle STCH continuous production system.

Figure 3. Daily variability of GHI and DNI in Daggett (CA). (a) Solar zenith angle daily variation for summer and winter solstices, and equinoxes. (b) Representative spring cloudy day (March 31, GHI = 3.87 and DNI = 1.31 kWh m⁻² d⁻¹). (c) Representative summer sunny day (June 22, GHI = 8.91 and DNI = 11.65 kWh m⁻² d⁻¹). (d) Representative winter sunny day (December 22, GHI = 3.87 and DNI = 1.31 kWh m⁻² d⁻¹).
as well as dotted catalyst islands have been explored as viable approaches for efficient PEC devices for minimization of the parasitic light absorption. While the uniformly coated catalyst layer would vary the same geometric area of the light capture area, the dotted catalyst islands could reduce the geometric area coverage by several orders of magnitude.\textsuperscript{62,63} As a result, these designs with low filling fractions of electrocatalysts can significantly reduce the usage of precious metals. However, high-cost materials, such as RuO\textsubscript{2} and IrO\textsubscript{2} even though they are stable and highly active for the oxygen evolution reaction in acid, are typically not encouraged for use in such systems due to the cost and scalability.\textsuperscript{64} In contrast, STCH reactors require high concentration factors (at least 2500) to limit re-radiation losses (~T\textsuperscript{4}) that added to the collection losses, which are inclusive of optical losses, makes the collection area >5000 times larger than the receiver aperture area. The collected sunlight after the receiver focal point defocuses (generally) before falling on and being absorbed by the active materials in the reactor, which effectively has an absorbing flux at C > 200−500. In addition, the design context for a STCH reactor is typically for a centralized \( H_2 \) production plant; due to the balance of system cost, a minimal plant size is likely 1MW. In contrast, PEC owing to the panel-like modular design analogous to a PV panel, can be distributed with flexibility of plant size depending on the end use of the \( H_2 \).\textsuperscript{49} While both will benefit from economies of scale, the expectation is that the minimum scale will differ between the two.

## SUNLIGHT UTILIZATIONS OF PHOTOELECTROCHEMICAL AND SOLAR THERMOCHEMICAL SYSTEMS

While both PEC and STCH use sunlight to drive the water-splitting reaction, the sunlight utilization in each case is distinctively different. Direct normal irradiance (DNI), which is the power received on a unit area at the Earth’s surface from the sun without having been scattered by the atmosphere, is the input sunlight power used for STCH, while global horizontal irradiance (GHI) represents the total amount of direct and diffuse radiation received from above by a horizontal surface is often used as the input sunlight power for PEC:

\[
\text{GHI} = \text{DHI} + \text{DNI} \cos(z)
\]

where \( z \) is the solar zenith angle and DHI is the diffuse horizontal irradiance (power received on a unit area received from above by a horizontal surface DHI that does not arrive on a direct path from the sun). In sunny days, the DNI term represents up to 70−90% of the total irradiance; however, it is negligible on cloudy days.\textsuperscript{65} The seasonal and daily variation resulting in larger \( z \) explains the higher annually average of DNI than GHI. As an example, Figure 3 illustrates this variation at Daggett (CA) based on hourly TMY2 (second edition of the typical meteorological year) data. The maximum annual variation in zenith angle occurs between the summer and winter solstices in nontropical areas as Figure 3a shows. At noon, the cosine factor attenuates the DNI in the GHI by 2% at the summer solstice and 47% at the winter solstice. This cosine factor explains the difference between DNI and GHI peaks in Figure 3c,d. Figure 3b shows the relevance of diffuse light during a cloudy day sometimes dominating GHI. The annual GHI and DNI in this representative sunny location are 2138 and 2791 kWh m\textsuperscript{-2}, respectively.

The preferred deployment sites for STCH or PEC is similar to concentrating solar power (CSP) or a traditional fixed PV panel, respectively. Only high insolation regions are preferred locations for STCH deployment with a recommended minimum annual DNI \( \approx 2365 \text{ kWh m}^{-2} \text{ yr}^{-1} (6.5 \text{ kWh mg}^{-2} \text{ d}^{-1}) \) and latitudes between 23 and 40° (north or south).\textsuperscript{56} PEC offers more flexibility with locations owing to the contribution of diffuse light; however, locations closer to equator are beneficial with the lower zenith angle when tilt-tracker is not incorporated. The land-use requirements between PEC and STCH are comparable in the generation weighted average land use, and would likely follow a similar relationship as between PV and CSP.\textsuperscript{67}

The AM 1.5G spectrum with an integrated power of 1000 W/m\textsuperscript{2} is typically the standard input power spectrum for PEC cells. Both direct normal irradiance and diffuse (sky and ground reflected) contribute to the spectrum, collectable, in principle, from unconcentrated PEC device architectures. However, PEC devices coupled with solar concentrators with low concentrations would only be able to use the DNI, like STCH. In addition, depending on the light absorber materials, typical PEC devices only use part of the spectrum namely those photons with energies above the bandgap of the semiconductor materials, e.g., with enough energy \( E_{\text{ph}} \geq E_g \). While the material strongly absorbs photons with energy much greater than the band gap, the resulting photogenerated electrons and holes typically thermalize back down to band edges before being transported to catalytic sites to drive fuel forming reactions, which translates to an energy loss. Figure 4a

![Figure 4. AM 1.5G spectrum with the band gaps of the dual-junction light absorber defining the wavelength region of interest for the PEC system (pink color for top cell and green color for bottom cell).](https://doi.org/10.1021/acsenergylett.1c00758)
blocking, atmospheric attenuation, and receiver spillage. A total of 40–60% of the collected energy reaches the external surface of the receiver aperture, and of that, 5–35% is lost from re-radiation and convection with the environment due to the high temperature in the solar receiver (reduction reactor). Note that re-radiation and convection losses are highly dependent on the temperature and the concentration ratio, as shown in Figure S1. Due to these energy losses before any radiation can reach the PEC or STCH, as well as Daggett, for example, 95% of the available solar energy is above this threshold value.

SOLAR-TO-HYDROGEN CONVERSION EFFICIENCY DEFINITION OF PHOTOELECTROCHEMICAL AND SOLAR THERMOCHEMICAL SYSTEMS

Among various performance metrics, the solar-to-hydrogen (STH) conversion efficiency is one of the most important parameters in determining the levelized hydrogen production cost. In particular, high STH conversion efficiency alleviates the land requirements for a given hydrogen production capacity (e.g., kg/day) and lowers the balance of system cost. In both PEC and STCH systems, the STH conversion efficiency is not only dependent on the active materials, but also on the cell or reactor designs. For STCH, the STH also depends strongly on the mirror collection configuration, which determines the collection efficiency. The most efficient is not necessarily the most cost-effective, which is an important consideration.

The definition of the STH conversion efficiency is the ratio of the work that the chemical product (hydrogen) can perform to the overall energy input (solar) to produce the product. Here, we conceptually include a fuel cell at the exit of both semiconductor based devices. The energy requirements in devices (particle-based devices or planar catalyst coated semiconductor based devices). The energy requirements in PEC and STCH, as shown in Figure S1, due to these energy losses before any radiation can reach the PEC or STCH, as well as Daggett, for example, 95% of the available solar energy is above this threshold value.

Table 1. Lists of Standard Gibbs Free Energy of Formation ($\Delta G^0$), Standard Enthalpy of Formation ($\Delta H^0$), Vaporization Energy ($W_{\text{vap}}$), and Isothermal and Adiabatic Compression Energy ($W_{\text{comp}}^{\text{iso}}$ and $W_{\text{comp}}^{\text{adi}}$). Confusion with values and definitions can lead to mistakes in calculation of the STH efficiency or incorrect comparisons. We also converted the energies into different units to make the comparison as clear as possible.

<table>
<thead>
<tr>
<th>$T$ (K)/$P$ (bar)</th>
<th>phase of water</th>
<th>$\Delta G^0$ (kJ/mole)</th>
<th>$\Delta H^0$ (kJ/mole)</th>
<th>$W_{\text{vap}}$ (kJ/mole)</th>
<th>$W_{\text{comp}}^{\text{iso}}$ (kJ/mole)</th>
<th>$W_{\text{comp}}^{\text{adi}}$ (kJ/mole)</th>
</tr>
</thead>
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<tr>
<td>298/1</td>
<td>liquid</td>
<td>237.1</td>
<td>32.7</td>
<td>1.23</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>298/1</td>
<td>liquid</td>
<td>285.8</td>
<td>39.4</td>
<td>1.48</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>298/1</td>
<td>gas</td>
<td>228.6</td>
<td>31.4</td>
<td>1.18</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>298/1</td>
<td>gas</td>
<td>241.8</td>
<td>33.3</td>
<td>1.25</td>
<td>400</td>
<td>300</td>
</tr>
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<td>298/1 to 398/350</td>
<td>gas</td>
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<td>6.1</td>
<td>0.23</td>
<td>400</td>
<td>300</td>
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<tr>
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<td>38.3</td>
<td>5.3</td>
<td>0.20</td>
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<td>300</td>
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</table>

*The pressure of 350 bar is commonly applied in fuel cells.*

formation for liquid water ($\Delta G^0_l$) and water vapor ($\Delta G^0_{vap}$), the standard formation enthalpy for liquid water ($\Delta H^0_l$), or the higher heating value of hydrogen, HHV) and water vapor ($\Delta H^0_{vap}$, or the lower heating value of hydrogen, LHV), vaporization energy ($W_{\text{vap}}$), and isothermal and adiabatic compression energy ($W_{\text{comp}}^{\text{iso}}$ and $W_{\text{comp}}^{\text{adi}}$). Confusion with values and definitions can lead to mistakes in calculation of the STH efficiency or incorrect comparisons. We also converted the energies into different units to make the comparison as clear as possible.

We define the STH conversion efficiency for both systems, PEC and STCH, as

$$\eta_{\text{STH}}(\text{PEC and STCH}) = \frac{n_{H_2} \Delta G^0_l}{Q_{\text{solar}}}$$

where $n_{H_2}$ and $m_{H_2}$ are the amount of hydrogen produced over a unit of time in mol and kg, respectively, $\Delta G^0_l$ is the Gibbs free energy of water formation in the liquid phase, and $Q_{\text{solar}}$ is the incident solar energy over the same unit of time. Note that the maximum net work that can be extracted from the chemical product is defined by $\Delta G^0_l$. When the purpose of the $H_2$ is the heat of combustion as opposed to net work, then that can be extracted from it, HHV (if the water condenses in the process) or LHV (if the water does not condense in the process) should be used in the STH leading to higher efficiencies than the maximum work metric. Equation 12 shows the instantaneous STH conversion efficiency:

$$\eta_{\text{STH,inst}} = \frac{n_{H_2} \Delta G^0_l}{Q_{\text{solar}}}$$

where $n_{H_2}$ and $m_{H_2}$ are the molar and mass flows, respectively, of hydrogen produced at this specific moment and $Q_{\text{solar}}$ is the incident solar flux.

In PEC systems, $Q_{\text{solar}}$ is defined as the total solar energy that reaches the photoactive part of the PEC device. We note that the sunlight collection area in PEC devices is often comparable to the photoelectrochemically active area. The instantaneous STH conversion efficiency device is often evaluated as follows:

$$\eta_{\text{STH,inst(PEC)}} = \frac{\Delta U_{\text{ran}}}{P_{\text{light}}}$$

where $J_{\text{ran}}$ is the PEC operating current density at 0 V vs counter electrode potential, $\Delta U_{\text{ran}} = 1.23$ V is the thermodynamic potential for water-splitting, $J_{\text{FE}}$ is the Faradaic efficiency, and $P_{\text{light}}$ is the incident light irradiance. Equation 11 is often used to evaluate the daily or annually averaged STH conversion efficiency for PEC devices.

From the energy efficiency point of view, the vast majority of the energy loss in the PEC system takes place within the PEC devices (particle-based devices or planar catalyst coated semiconductor based devices). The energy requirements in
the balance of system (BOS) for the PEC system are low. For example, optical components or heat management would not be needed for unconcentrated PEC devices at the system level. The energy requirements for pumping or circulation of electrolytes within PEC devices are minimal at the system level. In addition, the product separation, which could require significant energy inputs in STCH, is often not a concern and would not need additional energy inputs in PEC systems due to the incorporation of membrane separators. As a result, scaling up of PEC devices can often be achieved by multiplexing and connecting unit cells, and this approach was demonstrated in literature showing comparable performance as a single cell.72,73 Note that while the energy requirements for PEC’s BOS is low, the cost related to BOS is not necessarily low.

In STCH systems, the energy used to produce the hydrogen necessarily includes energy collected by the concentrating mirrors (typically a heliostat field but can also be a parabolic dish concentrator) to project redirect the sunlight into a receiver, but can include an additional contribution of energy to cover a series of the parasitic loads needed to drive the process. Among these loads, the most significant are the receiver oxygen removal, the H2–H2O separation work, and the steam generation. Depending on the chosen operating conditions, the energy recovery system can or cannot cover the total demand of energy. Thus, when internal heat is insufficient, then it is necessary to include these added energy contributions in the STH definition. Note that the primary energy resource to provide these parasitic loads may or may not be from a solar origin, but for practical reasons it is considered solar as the solar equivalent in the STH definition. Hence, the STCH community often expresses the STH conversion efficiency as follows:

$$\eta_{\text{STH(STCH)}} = \frac{n_{\text{H}_2} \Delta G_{\text{H}_2}^0} {Q_{\text{solar}} + Q_{\text{aux}}}$$

(14)

where $Q_{\text{solar}}$ is the incident solar energy calculated as the integral of incident solar flux over the time duration analyzed and $Q_{\text{aux}}$ is the added energy input to cover the parasitic loads of the process over the same time duration. There is no consensus in the STCH community regarding $Q_{\text{solar}}$. Some researchers include the process of solar collection and others not. To make a fair comparison with PEC systems, we define $Q_{\text{solar}}$ as the total solar energy that reaches the collection area; therefore, the collection losses and receiver re-radiation and thermal losses are included in this definition.

It is important to note that, while different definitions of the solar-to-hydrogen conversion efficiency have their own merits in guiding the development of the technology in the field, simple comparisons between these efficiency numbers with different definitions could be misleading.

It is important to note, that while different definitions of the STH conversion efficiency (for example, the different expression of STH conversion efficiency in eqs 11 and 14) have their own merits in guiding the development of the technology in the field, simple comparisons between these efficiency numbers with different definitions could be misleading. In addition, while the Gibbs free energy, which represents the maximum extractable net work from the chemical products, should be used in the numerator in the efficiency definition, the use of $\Delta G^0$ or $\Delta G^0$ depends on the phase of the water at the system boundary. To compare between PEC and STCH, we consider various power losses as the input power from sunlight goes through the PEC and STCH system. For PEC, we examined the loss mechanism in a high-efficiency PEC device14 as illustrated in Figure 5a,b. See details of the quantification in Figures S2 and S3.

Figure 5a starts from a standard AM1.5G illumination with solar power of 1000 W m$^{-2}$ as design point (DP). Since the photoabsorber can only absorb photons with energies greater than the specific bandgap, for the InGaP/GaAs tandem cell, 729 W m$^{-2}$ of power is usable, which corresponds to 27.1% loss from the spectrum below bandgap.14 The second power loss originates from the less than perfect reflectivity due to the materials in the optical pathway, such as catalyst or protective layers. In this case, an additional 7.4% is lost leading to 655 W m$^{-2}$ in the remaining power.14 The third power loss comes from the thermalization and recombination loss within the photoabsorber at the operating voltage and current density. For the PEC assembly using InGaP/GaAs tandem photoabsorber and RuO$_2$/Rh NP catalysts for OER and HER, the operating current density, voltage, and resulting power are 15.7 mA cm$^{-2}$, 1.93 V, and 303 W m$^{-2}$, respectively.14 The calculated thermalization and recombination loss is 35.2% of the total incident solar power. The energy output of PEC water-splitting device is then limited by Gibbs free energy of water formation. Hence, the last power loss can be contributed to catalysis loss from the overpotentials for water-splitting catalysis as well as polarization losses such as resistive loss due to ionic transport in the PEC device. With the addition of 11% electrocatalysis loss of the total incident solar power, the resulting hydrogen generation power from in the reported PEC assembly is 193 W m$^{-2}$, leading to a 19.3% STH conversion efficiency.14

The thermalization and recombination loss is the major loss that is constrained by the detail balance limit (or Shockley–Queisser limit). However, bandgap optimization can improve the device efficiency. Note that further reduction of the electrocatalytic loss based on RuO$_2$ (for OER)/Rh NP (for HER) catalysts will result in minimal improvement in the STH conversion efficiency of the PEC assembly using InGaP/GaAs tandem photoabsorber based on the load curve analysis (see Figure S2). Replacing the catalysts with nonprecious metal catalysts will further increase the electrocatalytic losses and also results in significant decrease in the STH conversion efficiency of the system because the operating points move sharply beyond the maximum power point of the PV curve. Different tandem structures or triple junction cells with optimal combination of bandgap values would be desirable to accommodate reduction of the electrocatalytic activity of the catalysts.74 Figure 5b shows our results from an annual average based on GHI irradiance in Daggett (CA). Starting with average solar power of 244 W m$^{-2}$, the 27.1% below bandgap photon loss leads to remaining power of 178 W m$^{-2}$. After
considering 7.4% from reflection loss, we obtain a power of 160 W m$^{-2}$. With the additional thermalization and recombination loss of 36.1%, 72 W m$^{-2}$ remains to contribute to hydrogen generation. Lastly, we account for the 10.2% electrocatalysis loss. As the production rate of hydrogen scales linearly with the solar illumination in the optimized coupling between the light absorber and catalysts, the annual averaged STH conversion efficiency in the system considered here...
yielded the same STH efficiency as the instantaneous STH conversion efficiency at the DP of 19.3%, with the hydrogen generating power going down to 47 W m$^{-2}$, corresponding to an annual 411 kWh m$^{-2}$ yr$^{-1}$. In other words, the losses are not dependent on the absolute illumination, in contrast to STCH, where some losses scale with illumination and others are fixed independent of illumination. Hence, the annual average efficiency in STCH differs from peak efficiency noticeably (see below).

As pointed out earlier, the high STH conversion efficiency does not necessarily lead to the low cost of H$_2$. Si-based cells in particles) STCH system with CeO$_2$ as the redox-active material (see Figure 6). In the analyzed system, the active absorption (ideally the material is close to a perfect absorber), which causes the material to heat and as it heats the absorbed energy is necessarily exposed to the environment.68 At the DP, the sum of the receiver losses depends on the concentration ratio and the re-radiation temperature; with the assumptions here (1700 °C and 5000 suns, which is equivalent to 5 MW m$^{-2}$) is ~18.4% of the total irradiance, hence the irradiance that reaches the redox-active material is ~647 W m$^{-2}$. The material absorbs the radiation (ideally the material is close to a perfect absorber), which causes the material to heat and as it heats the redox-active off-stoichiometric metal oxide reduces and releases oxygen (electrons from the oxygen anion stay behind and find a receptive cation to reduce). The absorbed energy is necessarily more than enough to split water. Hence, the second reaction step is exothermic.

The balance of system has a number of energy consuming processes that are important in estimating an overall system efficiency. Among the inevitable energy consumption of the system are the $\Delta H$ of reduction for the material and the free energy of mixing of the gases (N$_2$/O$_2$ and Steam/H$_2$). However, since the unit operations of O$_2$ and H$_2$ separations occur at lower temperatures than the reoxidation temperature, the rejected heat (and exergy) from the reoxidation exotherm. Therefore, $\Delta H$ of reduction is the minimum energy needed to drive the thermochemical process. Considering only this energy expenditure, the thermochemical process efficiency is ~51.7% accounting for 31.2% of the losses of the total irradiance. Note that this value is dependent on the active material, here ceria, and the operating conditions of the system. Including realistic separation inefficiencies and heat transfer exergy destruction, the thermochemical process efficiency drops to 34.6%. The heat recovery here reuses the unrecovered particle sensible heat in the solid—solid heat exchanger and the exothermic heat of reaction released in the reoxidation to heat the reactants and to supply the energy demand of separations of the product gases O$_2$ and H$_2$ from
nitrogen and excess steam, respectively. When this energy balance is not sufficient, then an input of energy must be added ($Q_{\text{inj}}$) which in this example was not necessary.

Figure 7 shows the internal energy distribution for a STCH system based on ceria at the DP and inevitable inefficiencies. In this example, the heat absorbed in the receiver is divided into three terms: one to provide the reduction endotherm to make the reaction possible (43.3% of total) and two to compensate for imperfect heat exchanger effectiveness heating both the sweep gas and metal oxide to the reduction temperature (1.2% and 20.3% of the total energy input for the gas and solid, respectively). The metal oxides carry the energy captured in the reduction reactor to the reoxidation reactor. Here, we can account for four terms: one part is used to produce hydrogen (22.4%), a second part is the heat released by the exothermic reaction (18.5%), a third part is sensible heat released to compensate for imperfect heat exchanger effectiveness on cooling (20.3%), and the final part is second law necessary loss in heat to H$_2$ conversion (2.4%). The heat not converted into H$_2$ in the reoxidation step is available to drive all the remaining auxiliary processes at lower temperature than the reoxidation temperature.$^{,5,8}$ In our example here, the vaporization of the water consumed in the reoxidation is 3.8% of the total energy input. The heating of this steam and the recycled steam from the steam–H$_2$ separation process to the reoxidation temperature is 3.7% and 1.3% of the energy expenditure, respectively. The separation of the H$_2$ and O$_2$ consumes 4.8% and 1.4% of the total energy input, respectively. The remaining energy is rejected heat, which accounts for 26.1% of the total energy consumption and is available for use in other processes such as electricity production.$^{7,8,3}$ At the end of the STCH process, the resulting H$_2$ generation power in the selected STCH system is 224 W m$^{-2}$, leading to a 22.4% STH peak conversion efficiency. Other redox-active materials with lower DeltaH of reduction than ceria could lead to higher STH conversion efficiencies.

When the DNI is lower than the DP (i.e., 1000 W m$^{-2}$), the efficiency decreases because some losses are constants and do not scale with the DNI. Figure Sd shows our results from an annual average based on DNI irradiance in Daggett, California. Starting with average solar power of 319 W m$^{-2}$, the annual average STH conversion efficiency for this ceria example is 19.7%. Due to energy losses in the process, the system requires a minimum insolation level to operate. Taking a conservative value of 300 W m$^{-2}$, ~95% of the available solar energy is above this minimum threshold. The annual collection losses account for 21.0% of the total energy input. Heat losses from the receiver increase when the concentrated irradiance is under the DP DNI; hence, the annual average receiver losses increase to 22.1% of the total losses. The thermochemical process efficiency remains constant because a well-designed operating control system would adjust the particle flow to the amount of radiation and because we are not considering losses from thermal inertia in the reactors and heat exchangers at this level of analysis. The annual thermochemical process losses account for ~37.3% of the total annual energy input.

If the solar technology used for the energy collection is a heliostat field with a solar tower instead of a parabolic dish, the efficiency will be lower for both the DP and the annual basis, due to several factors. Among these factors, most significant are the cosine effect factor for the heliostat field (i.e., the reduction of the effective reflection area because heliostats do not point directly at the sun), the atmospheric attenuation, the shading and blocking of the heliostats at some solar angles, and a higher receiver spillage (lower interception). The typical collection efficiency at the DP is 60%, and the concentration ratio for thermochemical applications is 3000 (sometimes including secondary concentrators, with additional collection losses; hence, there is a trade-off between collection efficiency and receiver efficiency when determining the optimal concentration factor for performance and cost). The major factor in designing an optimized heliostat field layout is the cosine `efficiency' of the heliostat. This efficiency depends on both the sun’s position and the location of the individual heliostat relative to the receiver. A tracking mechanism positions the heliostat so that its surface normal bisects the angle between the sun’s rays and a line from the heliostat to the tower. The effective reflection area of the heliostat, as a result, is reduced by the cosine of one-half of this angle. A less-optimistic scenario of the STCH based on heliostat field technology, a reduction temperature of 1500 °C, and a solid–solid effectiveness of 70% is included in Table S1. Figure S4b evaluates this less-optimistic scenario resulting in a 5.8% STH conversion efficiency at the DP. However, it is important to highlight that CeO$_2$ is too difficult to reduce and the extent of reduction at 1500 °C is low, penalizing the system performance. Other materials with better reduction capability could significantly increase this STH conversion efficiency, which is where much of the forefront research is ongoing.

Another figure of merit to use for the conversion efficiency for both technologies is the energy utilization number, which refers to the total energy required to produce 1 kg of H$_2$ at standard temperature and pressure.

Another figure of merit to use for the conversion efficiency for both technologies is the energy utilization number, $U = \frac{Q_{\text{inj}} (\text{kWh})}{m_{\text{H}_2} (\text{kg})}$, which refers to the total energy required to produce
Table 2. Summary of Operating Conditions for PEC and STCH Systems

<table>
<thead>
<tr>
<th></th>
<th>photoelectrochemical (PEC)</th>
<th>solar thermochemical (STCH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>operating temperature</td>
<td>5 to 80 °C</td>
<td>reduction: 1350–1800 °C</td>
</tr>
<tr>
<td>illumination intensity</td>
<td>0 mW cm(^{-2}) to 1 W cm(^{-2}) up to 47.4 W cm(^{-2})</td>
<td>reoxidation: 600–1250 °C</td>
</tr>
<tr>
<td>water condition and utilization</td>
<td>liquid or water vapor at ambient T and (P_f) recirculate water/electrolyte during operation</td>
<td>focal point: (C \approx 2500–5000) suns (2.5–5 MW m(^{-2})) absorbing material: 20–50 W cm(^{-2})</td>
</tr>
<tr>
<td>hydrogen output</td>
<td>humidified H(_2) at ambient temperature (before separation)</td>
<td>steam at or below the oxidation temperature and typically 1 bar, use water–steam transformation, preferred 90% steam or below after reaction; recirculate the excess steam after separating the H(_2) operation</td>
</tr>
<tr>
<td>impact of partial pressure of O(_2)</td>
<td>10(^{-1}) bar (corresponds to 240 mV)</td>
<td>H(_2)–steam mixture (0.1 bar or higher) at the oxidation temperature (before separation)</td>
</tr>
<tr>
<td>capacity factor</td>
<td>24.4% in Daggett, CA, generally ~15–30% constrained by the lowest rate of reduction and oxidation</td>
<td>28.1% in Daggett, CA, without storage, preferred range 25.7–100%</td>
</tr>
<tr>
<td>spatial and temporal constraints</td>
<td>essentially constrained by the lowest rate of reduction and oxidation</td>
<td>two different reduction and reoxidation reactions that are spatially or temporally separated; different reduction and reoxidation rates possible</td>
</tr>
<tr>
<td>potential sites</td>
<td>potentially deployable over oceanwater, PV screening</td>
<td>DNI &gt; 6.5 kWh m(^{-2}) day(^{-1}); land use; CSP screening</td>
</tr>
</tbody>
</table>

1 kg of H\(_2\) at standard temperature and pressure. For the InGaP/GaAs cell with 19.3% STH conversion efficiency, \(U = 183\) kWh kg\(^{-1}\) H\(_2\). With the annual GHI of 2138 kWh m\(^{-2}\) in Daggett, CA, an average H\(_2\) production rate of 0.032 kg day\(^{-1}\) m\(^{-2}\) is feasible. It is important to note that the energy utilization number is also dependent on the final state of the H\(_2\); for instance, Table 1 shows a calculated difference of 3.3 kWh kg\(^{-1}\) H\(_2\) between H\(_2\) at 1 and 350 bar in an adiabatic pressurization process. For a STCH system with 19.7% annual STH conversion efficiency, \(U = 166\) kWh kg\(^{-1}\) H\(_2\). With the annual DNI of 2791 kWh m\(^{-2}\) in Daggett, CA, an average H\(_2\) production rate of 0.046 kg day\(^{-1}\) m\(^{-2}\) is feasible; note that this result is for collection area, not for total land area.

### OPERATING CONDITIONS FOR PHOTOELECTROCHEMICAL AND SOLAR THERMOCHEMICAL SYSTEMS

Table 2 summarizes the differences in operating conditions between PEC and STCH systems. Most reported lab-scale PEC devices operate at room temperature under various illumination conditions without careful control over the operating temperature of the device. However, in the real-world PEC devices will likely need to operate above the freezing point of the electrolyte, or 80 °C under concentrated sunlight. The trade-offs of operating at elevated temperature have been investigated. In contrast, STCH systems require high illumination conditions (highly concentrated) to limit re-radiation from the high-temperature reduction reaction. However, that illumination is typically not the illumination onto the active materials. A minimum DNI threshold is typically necessary to ensure that the receiver does not hit a stagnation temperature lower than the desired reoxidation temperature. Note that the higher the concentration ratio, the lower the receiver re-radiation losses, but typically accompanied by a higher cost for the solar collection; therefore, it is a design parameter that should be optimized in a techno-economic analysis. In other words, the highest efficiency system is not necessarily the most cost-effective.

PEC devices use liquid water or water vapor as the input water feedstock. For liquid water, various types of electrolytes including acid, base, or near-neutral pH electrolytes have been employed, and each has its own advantages and disadvantages. In contrast, STCH systems use superheated steam typically at atmospheric pressure. The reoxidation reaction depends sensitively on both temperature and the amount of excess steam relative to available oxygen ion vacancies. The higher the reoxidation temperature, the larger the amount of excess steam needed to drive the reaction to near completion, whereas a lower reoxidation temperature requires a larger amount of sensible heat to be shed after the reduction step and then injected to raise the temperature of the metal oxide for the reduction step. Steam recirculation (avoiding the phase change as discussed above for PEC) and high heat recovery effectiveness are critical to reduce the heat system requirements.
The $\text{H}_2$ produced from PEC devices is often humidified, and additional processes will be required to remove the water vapor from $\text{H}_2$; however, the output $\text{H}_2$ is relatively pure, with minimal gas impurities such as $\text{O}_2$. In STCH systems, the production of $\text{H}_2$ is at the reoxidation temperature ($600−1250 \degree \text{C}$) in a mixture of excess steam. The process for separation of $\text{H}_2$ from the steam—$\text{H}_2$ mix contributes to the total energy consumption. Optimizing the temperature and approach to the $\text{H}_2/\text{H}_2\text{O}$ separation will be important; however, to date there has not been much research attention to this important part of the system. The lower the separation temperature, the lower the theoretical energy of separation. Nevertheless, the lower the separation temperature, the greater the demand on gas–gas heat recovery or recovery of the vaporization energy if the steam condenses. There is a reasonable consensus in the STCH community that avoiding the gas-to-liquid phase transition and doing the separation in the gas phase will require less overall energy demand. After separating the $\text{H}_2$, it will be necessary to pump it up to the required delivery pressure.

The partial pressure of $\text{O}_2$ in the anode chamber for the PEC device will change the equilibrium potential for OER, and as a result, the required total voltage for water-splitting will be reduced as the partial pressure of $\text{O}_2$ decreases in the anode chamber. For example, if the partial pressure of $\text{O}_2$ is $10^{-4}$ bar, the total voltage for the water-splitting reaction reduces by $\sim 240 \text{ mV}$ based on the Nernstian relation. Oxygen removal is another critical aspect of STCH systems. A reduced $\text{O}_2$ partial pressure is a requirement in the reduction reactor to increase the reaction extent for the oxides (as it increases the entropy production for the oxygen to go from bound in the lattice to the gas phase). The current metal oxide materials suggest partial pressures of $10−100 \text{ Pa}$ will be necessary (lower is desirable, but reducing the partial pressure has a number of associated challenges). Although lower partial pressures increase the extent of reduction (the amount of off-stoichiometry), it also introduces an engineering challenge, and considerations of the rapidly increasing volume flow will determine ultimate limitations. Vacuum pumping and inert gas sweeping are the main technologies to achieve these low oxygen partial pressures, and both have advantages and disadvantages discussed in the literature. Alternatives that are also being explored recently include thermochemical pumping and sorption pumping/separation.

The capacity factor, defined as the ratio between the actual energy output and output if operated at maximum capacity at all times, is quite similar for PEC and STCH, as they are both direct solar technologies and operate when the sun is shining. For PEC devices, the overall rate of $\text{H}_2$ production is constrained by the lower of the two rates, water oxidation or proton reduction. In other words, the OER at the anode and HER at the cathode must always be rate-matched. Note that it is possible to achieve a higher overall capacity factor of the PEC system with redox couples or redox carriers that separate HER and OER spatially and temporally to achieve $\text{H}_2$ production at night. PEC systems that produce $\text{H}_2$ and $\text{O}_2$ in two steps would share many system-level considerations with STCH systems.

For STCH, the reoxidation reactor and the reduction reactor can (but do not necessarily) operate at different rates, even in a continuous cycle. Furthermore, it is possible to store the reduced metal oxide (containing the oxygen vacancies) and reoxidize when the sun is not shining; however, doing so has implications for the heat integration and the metal oxide inventory in the design of the system, thus having efficiency and cost implications. Nevertheless, the capacity factor for STCH is constrained by the minimum annual DNI needed to build a cost-effective plant (desirable to have 6.5 kWh/m$^2$/day, but it will come down to the economics) and maximum storage capacity. Note that although a capacity factor of 100% is potentially achievable, the cost of the redox-active material and the insulation of the storage will likely be limiting and will determine viability.

**CHALLENGES AND OUTLOOKS**

Sustainable “green” hydrogen generation will be a crucial element for deep global decarbonization across multiple sectors in society. Low-temperature electrolysis (LTE) using alkaline (AEM) and proton exchange membrane (PEM) electrolyzers has recently received renewed interest in many countries; the largest alkaline electrolysis system was deployed in Aswan Dam at a capacity of 165 MW in the 1960s. While the direct solar-to-hydrogen technology pathways, including PEC and STCH, have a significantly lower technical readiness level (TRL) based on the demonstrated scale as well as the longevity of the demonstrated systems, there are unique aspects of these pathways when compared to LTE. For example, direct solar-to-hydrogen pathways can be advantageous in locations without reliable electrical grid infrastructures, as they can avoid electrical transmission lines and losses. For PEC water-splitting, the largest photoactive area demonstrated to date was $\sim 1 \text{ m}^2$, in which the highest hydrogen production rate of $\sim 0.65 \text{ g/day}$ and STH conversion efficiency of 0.4% were achieved with a fixed Al-doped SrTiO$_3$ photocatalyst system. Highly efficient PEC devices that incorporate legacy PV materials, such as Si and III–V semiconductors, exhibited STH conversion efficiency $>10\%$ and longevity of the device from tens to hundreds of hours of operation. For STCH, the largest demonstration facility is in the range of 750 kW, which had three fixed-bed reactors, with two containing NiFe$_2$O$_4$ and one with CeO$_2$ as redox-active materials; no efficiency has been reported for that demonstration. Experimentally, the maximum efficiency reported for a thermochemical cycle has been 5.25% in a 4.1 kW fixed-bed reactor with CeO$_2$ operated in a solar simulator. Among the redox-active materials for two-step STCH water-splitting, only ferrites and CeO$_2$-based materials have been demonstrated on a pilot scale, and only CeO$_2$ has shown excellent cyclability and longevity with hundreds of cycles.

>“While the direct solar-to-hydrogen technology pathways have a significantly lower technical readiness level based on the demonstrated scale as well as the longevity of the demonstrated systems, there are unique aspects of these pathways when compared to low-temperature electrolysis.”

In a PEC system, the discovery of durable, cost-effective, and efficient photoelectrodes remains the top challenge for this technology. Despite approaching 20% STH conversion...
efficiency, the stability of the state-of-the-art III–V tandem-based device still remains a limitation. Protecting the high-efficiency photoelectrodes that use traditional PV materials from corrosion in water-splitting conditions, \textsuperscript{14,17,96,103,106} and discovering new PEC-unique photocathodes or photoanodes with semiconductor/electrolyte junctions, are two strategic approaches to improve the performance of the photovoltaics.\textsuperscript{10,11,90} A portfolio of materials are available for efficient and relatively stable operation of OER and HER in all pH regions. Notably, Earth-abundant, mixed-metal oxides, such as NiFeO\textsubscript{4} are often good candidates for OER, and mixed metals, such as NiMo, are often good candidates for HER in alkaline conditions.\textsuperscript{90,105–108} However, discovery of efficient and stable OER catalysts with Earth-abundant materials in acidic conditions is not yet in hand.\textsuperscript{109} One unique requirement for optimal catalysts for PEC water-splitting is the optical transparency of the catalyst to facilitate efficient light collection; various strategies that optimize the light path through the electrolyte/catalyst/semiconductor interfaces can further boost the device efficiency and expand the materials selections.\textsuperscript{110–116} In addition, little is known about dynamic operations (diurnal cycles and bad weather days) and their impact on catalyst materials, which would be necessary to understand for real-world operation. For PEC devices, recent demonstrations of unassisted PEC water-splitting with various configurations exist, with STH conversion efficiencies that exceed 10% and device stability in the range of tens to hundreds of hours.\textsuperscript{117–118} However, significant challenges remain in bringing the current PEC scale (typically <0.01 g/day) to the bench scale (0.1 kg/day) or subscale (2 kg/day).\textsuperscript{72,73} In addition, standardization of device architectures and benchmarking conditions are important to meaningfully compare results and performances across different PEC materials from the research community.\textsuperscript{117} Developing long-term stability protocols and corrosion analysis at the component level and at the device level also remains top priorities for the PEC community for the near future.

For STCH systems, the discovery of a new redox-active material able to reduce the solar input requirements per mole of H\textsubscript{2} produced while preserving good water-splitting thermodynamic and kinetic attributes is the top challenge for this technology. Furthermore, this ideal redox-active material should show fast redox kinetics, high cyclability, high thermal stress resistance, high thermal and oxygen ion conductivity, and low cost.\textsuperscript{118} Currently, researchers in the field consider ceria the state-of-the-art, as it is the most investigated material and it exhibits very good reoxidation properties, excellent high-temperature stability, excellent cyclability, very good conductivities, and fast kinetics.\textsuperscript{100,119} However, ceria is too difficult to reduce, pushing the reduction temperature up to 1500 °C or higher, or requiring a very low O\textsubscript{2} partial pressure (e.g., very high sweep flows) to obtain an appreciable reduction extent under inert gas sweeping.\textsuperscript{38,40} On the other side, ceria is very easily reoxidized, allowing high H\textsubscript{2}O/H\textsubscript{2} conversion (>10%) at high reoxidation temperatures (>1000 °C). A material like ceria with lower reduction enthalpy change (e.g., 15% lower) and similar reduction entropy change or slightly lower would reduce more easily while preserving the adequate reoxidation thermodynamics and kinetics. However, keeping the solid-state entropy change in reduction similar to that with ceria while reducing the enthalpy change may or may not be possible.\textsuperscript{120} Next best will be to tune the enthalpy of reduction and maintain a significant solid-state entropy change.

Considering the STCH system design, the reduction of heat losses and heat requirements to the auxiliary systems would increase the overall system efficiency to approach theoretical values.\textsuperscript{79,121} An efficient heat recovery system is necessary to optimally select the temperature difference between the reduction reaction (O\textsubscript{2} production) and the reoxidation reaction (H\textsubscript{2} production) without adversely affecting the STH conversion efficiency and taking advantage of a higher reduction extent and higher water conversion yield (i.e., limiting the amount of excess steam). Developing an effective (cost and performance) solid–solid heat exchange is a challenging endeavor, and no one has yet demonstrated 80% effectiveness.\textsuperscript{57,59,60,122} Removing oxygen from the reduction reactor is the other auxiliary system technology receiving more attention, although not enough attention for real-world applications. Technological approaches to achieve the necessary low oxygen partial pressures must be energetically efficient and economically affordable. Currently, a second law efficiency of 10% in N\textsubscript{2}–O\textsubscript{2} separation is considered acceptable in electrically driven devices. The development of thermally driven oxygen adsorption/desorption cycles could increase the STH conversion efficiency by using internal and low-quality process heat.\textsuperscript{98} Although less studied, the H\textsubscript{2}/H\textsubscript{2}O separation process is also critical to achieve a high STH conversion efficiency. An ideal H\textsubscript{2}/H\textsubscript{2}O separation process would reuse the residual process heat from the reoxidation reactor and separate both substances in the gas phase, preventing the water phase change, as recovering the latent heat is typically a greater challenge than achieving high effectiveness gas–gas heat exchange, since >90% effectiveness for gas-phase recovery at high temperature has been reported in the literature.\textsuperscript{123–126} More generally, finding optimal operating conditions or the ideal discoverable material does not enjoy consensus in the field.

Due to the high solar fluxes and high temperatures, in STCH, the receiver/reduction reactor is one of the most risky and critical components of the plant. It should be fabricated with materials resistant to severe thermal shocks and be able to work under high-temperature and oxidizing environments, noting that the materials are releasing oxygen inside of the reduction reactor. Nevertheless, the materials, the reactors, the heat exchange and heat integration, and the separations each face challenges for the approach to achieve its potential. Most of the focus has been on finding a material that is as good as ceria where ceria excels, and better than ceria where ceria falls short (namely striking the optimal balance between difficulty to reduce and difficulty to reoxidize). The reoxidation reactor is less risky than the reduction reactor from the point of view of materials, as its operating conditions are milder. However, it is just as critical. The heat captured in reoxidation plays an essential role in the STH conversion efficiency, as it can be reused to drive all the auxiliary processes of the plant. Currently, no reactor design has this feature developed.

“Both photoelectrochemical and solar thermochemical water-splitting systems can be extended to other reactions, such as CO\textsubscript{2} reduction and N\textsubscript{2} reduction.”
Both PEC and STCH water-splitting systems can be extended to other reactions, such as CO2 reduction and N2 reduction. For PEC systems, CO2 reduction and N2 reduction share the same common half-reaction, e.g., oxygen evolution reaction (OER) to provide the needed protons for the reduction reactions. However, due to the low solubility of CO2 and N2 in aqueous solutions, the PEC device architecture for CO2 reduction and N2 reduction can be very different from water-splitting reactions. For example, gas diffusion electrodes, which can readily prevent the product crossovers for H2 and O2, would face additional challenges for liquid product separations in PEC CO2 reduction systems. For STCH systems, the cycles based on redox-active metal oxides directly apply to CO2 splitting and/or combined CO2/H2O splitting for CO/syngas production, respectively. Since the reaction Gibbs free energy of the CO2 splitting is lower than that of the water-splitting at high temperatures, these cycles are less energy-demanding than the water-splitting. Other applications of STCH systems include oxygen pumping, inert gas purification, and N2 production from air and take advantage of the oxygen affinity from the reduced (oxygen-deficient) metal oxide. The STCH principles extend to redox-active metal nitrites, which can release nitrogen from their structure to react with H2 and synthesize ammonia.

In summary, we have compared and evaluated two direct solar hydrogen production approaches, e.g., PEC and STCH, in terms of sunlight utilization, device architecture and reactor design, STH conversion efficiency, and operating conditions of each system. Direct solar hydrogen production, while not cost-competitive with nearer-term approaches using renewable electrons, such as LTE, can be a unique alternative and complementary approach in certain regions of the world where the electricity grid is not fully deployed. It can also provide more energy resilience solutions to long-term energy storage and has the potential to achieve low-cost hydrogen production.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c00758.

Details of the quantification and parameters for loss analysis for PEC and STCH; examples of more realistic/less-optimistic cases for PEC and STCH (PDF)

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**Notes**
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