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Opportunities to improve the net energy performance of photoelectrochemical water-splitting technology

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Abstract

The hydrogen energy provided by solar-driven photoelectrochemical (PEC) water splitting must be greater than the energy used to produce and operate the technology, as a fundamental system requirement to enable energetic benefits to society. PEC H₂ production will require significant advances from both basic scientific research and applied technology development, prior to manufacturing and field deployment. To identify opportunities and priorities, here we use prospective life-cycle system modeling to investigate the net-energy significance of six characteristics describing the PEC life cycle: (1) embodied energy of active cell materials, (2) embodied energy of inactive module materials, (3) energy intensity of active cell fabrication, (4) energy intensity of PEC module assembly, (5) initial energy use for production of balance-of-system (BOS), and (6) ongoing energy use for operation and end-of-life of BOS. We develop and apply a system model describing material and energy flows during the full life-cycle of louvered thin-film PEC cells and their associated modules and BOS components. We find that fabrication processes for the PEC cells, especially the thin-film deposition of active cell materials, are important drivers of net energy performance. Nevertheless, high solar-to-hydrogen (STH) conversion efficiency and long cell life span are primary design requirements for PEC systems, even if such performance requires additional energy and material inputs for production and operation. We discuss these and other system dynamics, and highlight pathways to improve net energy performance.

1. Introduction

A transition from fossil to renewable energy sources is required for reasons of environmental quality and energy security.¹ Globally, we are heavily dependent on fossil fuels for transportation, electricity, heat, and other energy services. The three types of fossil fuels—coal, oil and natural gas—currently supply about 82% of all global primary energy use.² Combustion of fossil fuels leads to a range of detrimental impacts, including climate change³ and human health effects.⁴ Furthermore, as fossil fuels are formed largely from decayed organisms that were alive hundreds of millions of years ago, they are non-renewable over time scales of interest. Long-term human development will thus require a transition to renewable energy sources.

Because most renewable energy resources are diffuse (such as solar and wind), the capture area needed to harness a significant energy supply must be extensive. Specifically for photovoltaic (PV) power, Ong et al.⁵ calculated that the average capacity-weighted direct land use required by US PV installations is 1.3 ha per GWh per year. At this land use rate, a PV facility would require about 100 km² of land area to produce the same amount of electricity made by a 1GW fossil fuel-fired plant operating with a 90% capacity factor. The extensive infrastructure needed over such a large area comes at a relatively high energy cost, leading to long energy pay-back times and modest life-cycle energy returns on investment for renewable energy facilities.⁶ This challenge is compounded by the intermittent nature of renewable energy supply, and the difficulty of storing large amounts of PV electricity for use over diurnal and annual supply cycles.

Photoelectrochemical (PEC) water splitting devices are intended to directly convert solar radiation into hydrogen, a storable fuel, at relatively high energy conversion efficiencies. If successfully deployed, a future PEC device could overcome the challenge of intermittency of solar resources, by directly producing a fuel that can be stored and used upon demand. Hydrogen offers many of the same advantages as hydrocarbon fuels but without the CO₂ emissions upon combustion. For vehicle transportation, hydrogen-powered fuel cells overcome many of the current limitations of battery technology such as range, weight and cost (though ongoing research and economies of scale may further improve battery characteristics.) Solar-to-hydrogen (STH) efficiency is a commonly used performance metric of PEC devices. As defined by Chen et al.⁷, STH efficiency compares the Gibbs free energy of the hydrogen produced by a device under zero external bias conditions, to the solar radiation incident on the device exposed to solar AM1.5G illumination.

While STH efficiency is an important metric for benchmarking and comparing device-level performance^{8,9}, it does not, by itself, indicate the overall energetic utility of a PEC technology, because it does not consider essential non-solar energy inputs to the system. These technological energy inputs, e.g. for material supply, manufacturing, operations, and end-of-life management of the system, may be significant. Appropriate metrics for system-level performance may be obtained through net energy analysis (Figure 1). The net energy of a system is the energy available for societal use, after subtracting the energy required to create and operate the technology. If the energy inputs to the system approach the usable renewable energy harvested by the system, its contribution to sustaining societal wellbeing becomes negligible.

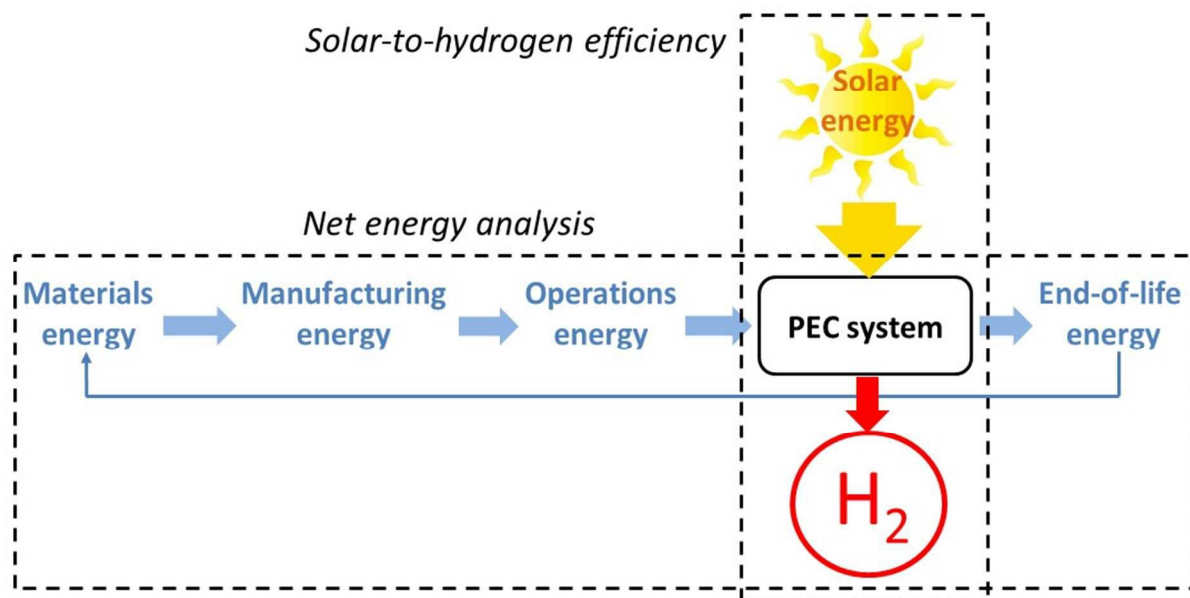


Figure 1. Solar-to-hydrogen efficiency compares the solar energy incident on a PEC cell to the chemical energy of the produced hydrogen. Net energy analysis compares the total technological energy inputs to the system (for material supply, manufacturing, operations, and end-of-life management) to the chemical energy of the produced hydrogen.

In previous studies, we have analyzed various aspects of net energy performance of PEC systems. Zhai et al.¹⁰ employed an innovative hybrid (bottom-up top-down) modeling approach to assess the device-level net energy balance of a silicon microwire PEC cell. Sathre et al.¹¹ added the balance-of-system (BOS) and end-of-life (EOL) energy effects to this cell design, producing the first system-wide net energy assessment of large-scale PEC hydrogen production. In the present analysis we build upon these

frameworks, to enable broader research questions. In this paper we introduce: (1) an innovative PEC cell and module architecture, with emphasis on large-scale manufacturability and operability; (2) more advanced analytical methodology, e.g. a novel method for estimating the embodied energy of a wide range of thin-film materials; (3) more refined technical design process, e.g. a rational reduction of materials used in PEC modules; (4) more thorough analysis of the energy implications of thin-film manufacture, considering a range of material combinations and deposition technologies.

We use prospective life cycle system modeling techniques to estimate the energy flows during the manufacture, operation and EOL of an eventual large-scale PEC water splitting facility and its supply chain, and we chart the opportunities for improving performance. Our goal is to identify key relationships and sensitivities across a range of materials and processes, rather than to find a single “correct” result. The early-stage life cycle modeling presented here is intended to generate knowledge to inform decisions made by materials scientists (e.g. performance targets for laboratory research), process engineers (e.g. design parameters for system scale-up), and policy makers (e.g. eventual net energy potentials of PEC systems). Combined with techno-economic analysis (e.g. ¹²), it provides a more robust basis for early-stage decision-making.

2. Methods

2.1 Modeling framework

Prospective life cycle system modeling is a method combining scenario analysis with consequential life cycle assessment (LCA), to evaluate the potential impacts of technologies and infrastructure systems that are not yet operating at commercial scale. It is intended to provide early-stage insights on opportunities and constraints of emerging technologies, to guide basic research toward effective innovation.

We begin the analysis by assuming a functional PEC technology with a given performance level. We then conduct a preliminary engineering design of a hypothetical large-scale PEC water splitting facility, including BOS. We then estimate energy requirements for materials, manufacturing, operation, and decommissioning of the facility. This provides us with information needed to calculate several net energy metrics describing the performance of the system. Furthermore, we apply this method using a range of plausible parametric values to identify sensitivities and quantify uncertainties. Overall, we seek opportunities to improve the life cycle net energy performance of the technology.

We develop and apply a prospective life cycle system model describing system-wide energy flows associated with a hypothetical utility-scale PEC energy facility with H₂ production equivalent to 1 GW annual average (1 GW higher heating value (HHV) annual average = 610 t H₂ per day). The 1 GW hydrogen production facility is configured on five hierarchical levels: cells, modules, panels, fields, and facility. The two smallest levels, the cell and module, are described in Section 2.2. The remaining three levels comprise the BOS and are described in Section 2.3. In particular, we investigate the significance of six key energy characteristics of PEC systems:

1. Embodied energy of active cell materials (semiconductors, catalysts, transparent conductive oxides (TCO), conductive substrate, protective layers, electrolyte, and membrane materials)
2. Embodied energy of inactive module materials (window, back cover, frame, and ribs)
3. Energy intensity of active cell fabrication (thin-film deposition processes and membrane manufacture)
4. Energy intensity of inactive module fabrication (cell and module assembly)
5. Initial energy use for production of balance-of-system (BOS) components
6. Ongoing energy use for operation and end-of-life of BOS components

The first two characteristics describe embodied energy of cell and module material supply, which account for energy used for extraction, primary processing, and transportation of materials to the PEC factory gate. The next two characteristics describe energy intensity of fabrication processes within the factory to produce finished PEC cells and modules. The final two characteristics account for the energy use by the BOS during production, operation and end-of-life of the facility. We quantify each of these characteristics in units of MJ of primary energy use per m² of active cell area. Together, these six characteristics comprehensively include energy use during the full life cycle of the technology. With reference to Figure 1, characteristics 1 and 2 correspond to Materials energy, characteristics 3, 4 and 5 correspond to Manufacturing energy, and characteristic 6 corresponds to Operations and End-of-life energy.

Our system model includes base-case values for each of the six characteristics, as well as high energy input and low energy input values corresponding to other possible configurations of a future large-scale physical system. The modeled high energy input, base case, and low energy input characteristics are described in Table 1. We conduct a sensitivity analysis by varying individual parameters from their base case values to their low input and high input values.

Table 1. Summary description of high energy input, base case, and low energy input characteristics of active cell, inactive module, and BOS components.

	High energy input	Base case	Low energy input
1. Active cell materials	<ul style="list-style-type: none"> • 250 nm GaAs photoanode • 250 nm InGaP photocathode • 120 nm TiO₂ protective layer • 1 nm Pt HER catalyst • 1 nm IrO_x OER catalyst • 100 nm ITO TCO layer • 20% material utilization • 2:1 precursor energy • 0.2 mm stainless steel substrate • 70 μm membrane • Electrolyte 	<ul style="list-style-type: none"> • 250 nm a-Si photoanode • 250 nm BiVO₄ photocathode • 60 nm TiO₂ protective layer • 1 nm Pt HER catalyst • 1 nm IrO_x OER catalyst • 50 nm FTO TCO layer • 50% material utilization • 1:1 precursor energy • 0.1 mm stainless steel substrate • 50 μm membrane • Electrolyte 	<ul style="list-style-type: none"> • 250 nm a-Si photoanode • 250 nm Fe₂O₃ photocathode • 30 nm TiO₂ protective layer • 1 nm Fe₃P HER catalyst • 1 nm NiFeOx OER catalyst • 10 nm FTO TCO layer • 80% material utilization • 0.5:1 precursor energy • 0.05 mm stainless steel substrate • 30 μm membrane • Electrolyte
2. Inactive module materials	<ul style="list-style-type: none"> • 2× 3 mm glass • Large PVC frame • PVC support ribs 	<ul style="list-style-type: none"> • 2× 2 mm glass • Medium PVC frame • PVC support ribs 	<ul style="list-style-type: none"> • 2× 1 mm glass • Small PVC frame • PVC support ribs
3. Active cell fabrication	Current typical thin-film coating	Current state-of-the-art inline thin-film coating	Solution coating at atmospheric pressure and room temperature
4. Inactive module fabrication	Base-case × 200%	From Zhai <i>et al.</i> ¹⁰	Base-case × 50%
5. Initial BOS production	Upper 90% confidence interval from Monte Carlo modeling	Adapted from Sathre <i>et al.</i> ¹¹ , see text	Lower 90% confidence interval from Monte Carlo modeling
6. BOS operation and EOL	Upper 90% confidence interval from Monte Carlo modeling	Adapted from Sathre <i>et al.</i> ¹¹ , see text	Lower 90% confidence interval from Monte Carlo modeling

In addition to the six life cycle system characteristics, we evaluate the effects on net energy of varying assumptions of cell performance, considering two key performance parameters: the service life span of the cells in use, and the solar-to-hydrogen conversion efficiency of the cells. Our base-case analysis assumes a cell life span of 10 years, and STH efficiency of 10%. We vary the life span between five and 20 years, and the STH efficiency between 5% and 20%. Due to paucity of data, we are unable to quantitatively link the variations in cell production energy and cell performance, though we conduct exploratory modeling investigations. This model can be refined as laboratory research and industrial

capabilities advance, to provide convergence to realistic technology performance. We assume that cell performance degrades linearly over time, with replacement occurring when STH efficiency falls to 80% of its original value. In our modeling this is characterized by a simple degradation factor, such that the average H₂ production over the life span of a cell corresponds to 90% of the nominal STH efficiency. We further assume 10% solar transmittance loss due to the combined effects of absorption, scattering and reflection by surface dust, encapsulation material, and electrolyte.

Across a range of values for the six system characteristics and two performance parameters, we calculate three net energy metrics. The *life cycle primary energy balance* describes how much usable net energy the facility provides to society during its lifespan. In units of PJ, it is calculated as the total energy output minus the total energy input:

$$\text{Energy Balance} = \{T \times E_H\} - \{E_P + (T \times E_O) + E_D\} \quad (\text{Eq. 1})$$

where T = Service life of the facility (years)

E_H = Energy (HHV) in hydrogen produced in 1 year (PJ/yr)

E_P = Energy used to produce the facility (PJ)

E_O = Energy used to operate the facility for 1 year (PJ/yr)

E_D = Energy used to decommission the facility (PJ)

The *energy return on energy invested* (EROEI, sometimes denoted as EROI) describes how much usable energy the facility will deliver, relative to its required energy inputs. A value without units, it is calculated as the total energy output divided by the total energy input:

$$\text{EROEI} = \frac{T \times E_H}{E_P + (T \times E_O) + E_D} \quad (\text{Eq. 2})$$

The *energy payback time* describes how long the facility must operate for it to deliver the H₂ equivalent of the energy required for its manufacturing, construction, and decommissioning. Note that energy payback time is not a life cycle metric as it does not consider the energy that continues to be delivered after the payback time is reached; the equation does not include the variable T , the facility service life. In units of years, energy payback time is calculated as the fixed energy inputs divided by the annual net energy output under full-scale continuous operation:

$$\text{Energy Payback Time} = \frac{E_P + E_D}{E_H - E_O} \quad (\text{Eq. 3})$$

2.2 Photoelectrochemical cell and module

There are a number of potential configurations for PEC cells and a number of different ways they could be classified. For example, they can be classified by their electrochemical architecture, the type and phase of reactants that they use, the products they generate, as wired or wireless devices, or some combination of these characteristics. A more complete description of various solar fuel-harvesting devices is given by Nielander et al.¹³

Wired devices are physically integrated, while maintaining chemical isolation between all parts of the photovoltaic cells and the electrolyte (e.g.¹⁴), or can allow contact between the electrolyte and the anodic or cathodic portion of a photovoltaic cell, while performing the corresponding cathodic or anodic reactions, respectively, on a separate wired electrode (e.g.¹⁵). Wireless devices perform electrochemistry directly on the photovoltaic cell's surfaces, either with or without some layer to protect the active semiconductor material from the chemical reactions (e.g.¹⁶). A more comprehensive list of lab-demonstrated wired and wireless hydrogen-producing devices is presented by Ager et al.⁹, which details notable demonstrated hydrogen-producing PECs. Within the wireless architecture, devices can be additionally characterized by the photoelectrode architecture. There are devices that use planar photoelectrodes¹⁷, ones that use suspensions of particulates to perform co-evolution of hydrogen and oxygen¹², and devices whose photoelectrodes are comprised of microwires.¹⁸ The distinction between wired and wireless devices is likely to be small in the context of a net energy analysis because of the small energy cost of wires, assuming that the manufacturing processes are similar for separate and integrated electrodes. The potential benefits in operational lifespan may be more significant. Additionally, many wireless devices are effectively wired due to their use of an ohmic contact rather than a semiconductor-liquid junction.

PECs can additionally be classified by the type and phase of the input reactant they use. Most wireless and wired devices use liquid water as a solvent to form an aqueous electrolyte that is in contact with the electrodes.¹⁴⁻¹⁸ Typically, the solute in the electrolyte is a strong acid or base that confers conductivity to the electrolyte to enable ion transport. In contrast, some PECs can operate using water vapor. The latter devices employ an ion conduction membrane in place of an aqueous medium in order to conduct protons

or hydroxyl ions from the anode to the cathode. Possible ways to design such vapor-fed devices are described by Xiang et al.¹⁹, and experimental demonstrations are described by Modestino et al.²⁰

Another way to classify PECs is by what products are generated in the cell. All of the demonstrated devices cited above generate hydrogen from water splitting. Electrochemically speaking, water splitting is easier to accomplish than reduction of carbon dioxide to produce hydrocarbon fuels.²¹ However, if a low overpotential catalyst were developed, this difference would be reduced. There are transport limits for carbon dioxide reduction reaction, but use of gas diffusion electrodes and/or high pressure can address these. There are several recent demonstrations of no-bias solar-driven carbon dioxide reduction (e.g.^{22,23}).

In this analysis, we consider a planar wireless device for water splitting in an aqueous electrolyte. Figure 2 shows cross-sections of the studied cell and module assembly at different scales. The overall module appears similar to a dual pane window with dimensions of 1 m × 1.2 m and thickness of 11 mm. A ribbed PVC frame is laminated between the glass panes and supports the louvered active cell assembly. Active thin-film layer stacks are angled within the louvered cell geometry, with a membrane mounted vertically in the structure such that it does not significantly reduce the illuminated active area.¹⁶ The oxygen and hydrogen evolution reactions are performed on opposite faces of the active device stack and the ion-exchange membranes separate the hydrogen and oxygen product gases. The thin-film device layers are also shown (not to scale) in Figure 2, and include a tandem photoabsorber, transparent conductive oxide (TCO) layer, protective anti-corrosion layer, and electrocatalyst layers for the oxygen-evolution reaction (OER) and hydrogen-evolution reaction (HER).

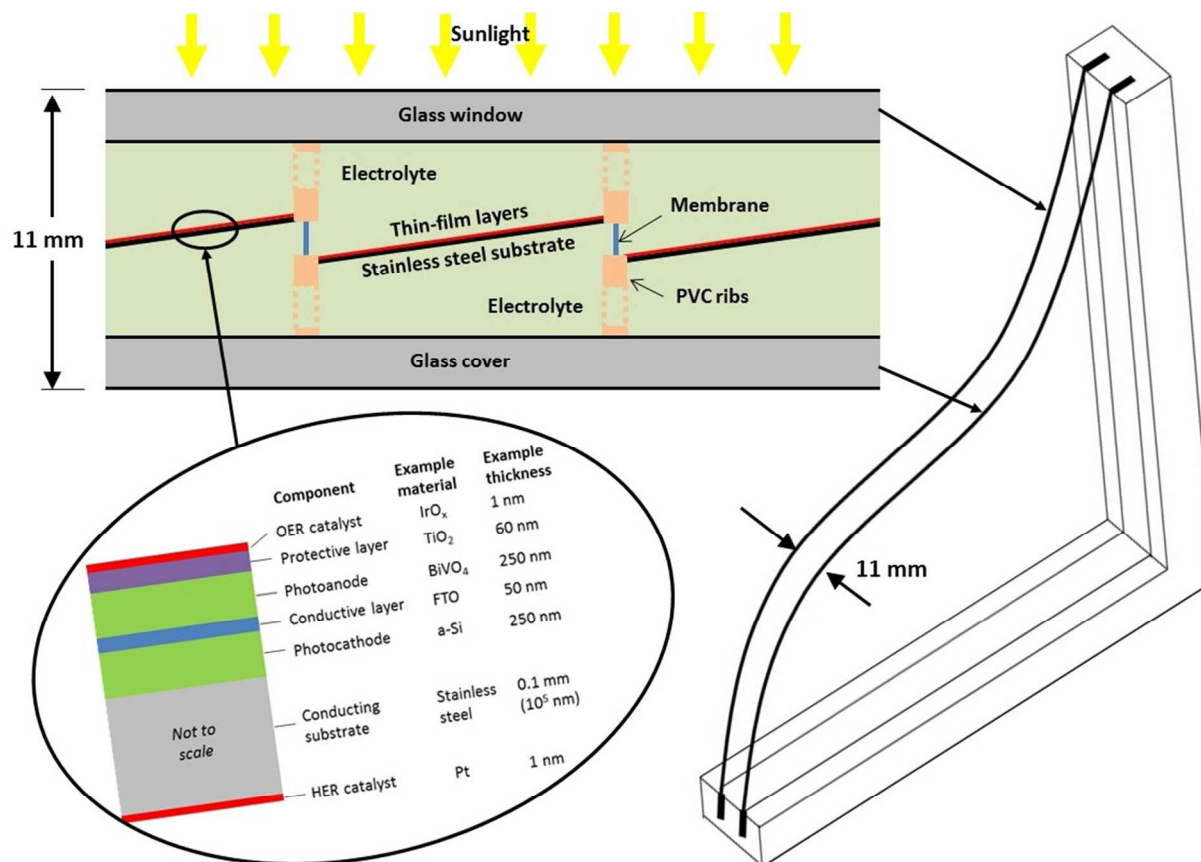


Figure 2. Cross-sections of PEC cell and module, including dual pane glass module encapsulation (right), louvered active cell configuration (top left), and thin-film layers of active cell materials (bottom left).

2.2.1. Embodied energy of active cell materials

This characteristic includes energy used for extraction, primary processing and transportation to the cell factory gate for the active device materials or their precursors. These materials include semiconductors, catalysts, transparent conductive oxide (TCO), conductive substrate, electrolyte, and membranes. Within the louvered geometry, we consider a generic electrochemical design with a range of potential active materials. Embodied energy describes the primary energy used for extraction, processing and transportation of materials. It does not include the energy used for thin film deposition within the PEC cell factory, which is described in Section 2.2.3. It also does not consider performance variations between materials in, for example, deposition energy intensity, product yield, STH efficiency, and cell life span.

Robustly quantifying the embodied energy of a diverse range of chemical compounds remains a challenge for the LCA community. Although standard life cycle inventory (LCI) databases (e.g. Ecoinvent, USLCI) contain embodied energy estimates for thousands of common commodity elements and compounds, they do not include data for tens of thousands of other specialty chemicals that are produced and used in smaller amounts. Many of the final or precursor materials of the thin films studied here are not represented in LCI databases or related literature. To overcome this challenge, in this analysis we use a simplified and generic approach. We estimate the embodied energy of precursor materials for thin film deposition using Equation 4:

$$\text{Thin Film Material Energy} = \sum_{\text{layers}}^i \sum_{\text{elements}}^j \frac{M_s \times E_s \times R_p}{F_m} \quad (\text{Eq. 4})$$

We sum over i layers of thin film, each containing up to j elements, and we quantify the embodied energy of each element based on 4 factors. The factor M_s is the specific mass, and quantifies the mass of the element per square meter of thin film layer [kg/m^2]. The factor E_s is the specific embodied primary energy of the refined element, i.e. the total energy needed to extract, process, transport and refine a unit mass of the element [MJ/kg]. The factor R_p is the ratio of the embodied energy of the refined element to that of the precursor material used in the deposition process, both measured per unit mass of the element. The factor F_m is the material utilization efficiency, and quantifies the mass of the element in the final thin film product per unit mass of the element in precursor materials delivered to the factory gate. R_p and F_m are both ratios without units, thus Equation 4 expresses the embodied energy of active cell materials in units of MJ of primary energy per m^2 of active cell area.

The specific mass M_s of materials deposited in each thin-film layer is calculated based on the layer thickness and the material density. Details on a range of thin film layers are listed in Table S1 of the Supplemental Information. In our base case we assume a 250 nm thickness for the photoanode and the photocathode, 200 nm thickness for the TCO layer, 60 nm thickness for the TiO_2 protective layer, and 1 nm thickness for the HER and OER catalysts. Within each deposited compound, we determine the mass of each element based on stoichiometry of the compound and atomic masses of the elements.

The embodied energy E_s of most refined elements is available from standard LCI databases. We base our calculations largely on embodied energy data from the Ecoinvent database²⁴, supplemented with data from Nuss & Eckelman.²⁵ The embodied energy of an element will likely depend on its purity; processing energy requirements increase significantly as the purity increases and allowable contaminant level

decreases.²⁶ Processes used to attain high purity materials include distillation, adsorption, ion exchange, filtration, and crystallization. In this analysis we use the default purity levels used in the Ecoinvent database²⁴, which typically represent the purest form of the element widely used in representative industries.²⁷

In some thin film deposition processes, the final deposited material is the same as the process raw material. For example, magnetron sputtering targets of a particular metal are used to deposit a thin film of the same metal. In many cases, however, the material composition of the finished thin film differs from the precursor materials used in the deposition process. For example, a TiO₂ protective layer may be applied from molecular precursors such as titanium isopropoxide or tetrakis(dimethylamido)titanium, using atomic layer deposition (ALD). Materials such as InP that are deposited by MOCVD are typically formed from other precursors, e.g. trimethyl indium and phosphine. Atmospheric pressure depositions also use non-elemental or oxide precursors; e.g. BiVO₄ can be deposited from bismuth nitrate and vanadium acetylacetonate. Thin films of indium tin oxide (ITO) can be formed by spray pyrolysis using InCl₃ and SnCl₄ precursors, and fluorine doped tin oxide (FTO) using SnCl₄ and NH₄F precursors. Amorphous silicon is typically deposited from a mixture of hydrogen and silane using plasma-enhanced chemical vapor deposition (PECVD). We account for this ambiguity with a factor R_p expressing the ratio of the embodied energy of the refined element to that of the precursor materials used in the thin film deposition process, both measured per unit mass of the element. We assume a base-case value of 1.0 for this ratio, with a range from 2.0 to 0.5. These values are justified and discussed in Section S2 of the Supplemental Information.

A final factor affects the embodied energy of cell material supply: The material utilization efficiency F_m expresses the mass of the element in the final thin film, per unit mass of the element in precursor materials delivered to the factory gate. This factor is determined by the material application yield (the percent of raw material element that is contained in finished thin films, the balance being wasted during the thin-film deposition process), the factory product yield (the percent of deposited thin film area in finished PEC modules, the balance being defective products), and the material recycling rate (the percent of waste element generated from material application and factory product yields that is recovered and reused). In practice, the material utilization efficiency will vary between deposition processes and materials, with gaseous precursor chemical reaction processes being the least material efficient and electrodeposition being the most material efficient. For example, Kreiger et al.²⁸ reported silane utilization of only 15% in conventional amorphous silicon deposition, but up to 83% utilization when silane is recycled instead of flared. Fthenakis²⁹ reported material utilization of only 34% for indium deposited by

co-evaporation during commercial CIGS thin film production, but up to 90% utilization via electrodeposition or by recovering residuals from vapor deposition. Alsema³⁰ reported a material utilization efficiency of 30-40% for sputtering deposition of TCO layers. Zweibel³¹ reported material utilization efficiencies of various thin film deposition processes: 10-25% for germanium applied as germane gas during amorphous silicon deposition, 50% for indium during CIGS evaporation deposition, 75% for indium during CIGS sputtering deposition, 75% for CdTe powder during commercial CdTe sublimation deposition, and 95% for tellurium during electrodeposition of CdTe thin films. Across this diversity of materials and processes, we assume a base-case material utilization efficiency of 50%, meaning that half of the sourced material is contained in the thin films of finished products, and the other half is wasted. We also consider values of 80% in our low energy input case, and 20% in our high energy input case. We assume that the factory product yield is high (approaching 100%) for all cases since business viability requires that defective products be minimal. We do not explicitly consider the energy implications of potential recovery and recycling of the wasted materials, which can be expected for high value materials such as platinum and iridium, but may not be economically viable for lower value materials such as iron and silicon.

Our base-case photocathode material is amorphous silicon, though other potential materials include InP and Cu₂O. Our base-case photoanode material is BiVO₄, a moderate bandgap photoanode, though other potential materials include a-Si, WO₃, Fe₂O₃ (hematite), and GaAs. Amorphous silicon is a buried junction device, meaning that, in principle, it can be incorporated to be photoanode or photocathode. If it is integrated with BiVO₄ or Fe₂O₃, one would expect it to be polarized so that its back, non-illuminated side is the HER electrode. If, on the other hand, it is integrated with InP, one would expect it to be polarized such that its back, non-illuminated side acts as the photoanode. Our high energy input case considers GaAs and InGaP photoelectrodes, and our low energy input case uses a-Si and Fe₂O₃ photoelectrodes. We acknowledge that not all combinations of materials we consider would have the required properties for effective PEC cells, e.g. sufficient photovoltage to split water, appropriate bandgap combination to achieve specified efficiency, and adequate stability against corrosion. Nevertheless, we consider them as representative examples in terms of embodied energy of a diverse range of materials and fabrication processes.

Potential HER catalyst materials for acidic or basic electrolyte solutions include Pt, NiMo, Co₂P, and Fe₃P. Potential OER catalyst materials for basic solutions include NiO_x, CoO_x, and NiFeO_x.³² For OER under acidic conditions, only IrO_x is currently available and new catalyst discoveries will be necessary to provide alternative materials. Our base-case analysis assumes the use of Pt for HER catalyst and IrO_x for

OER catalyst. The same materials are used in our high energy input case. Our low energy input case considers Fe_3P as HER catalyst and NiFeOx as OER catalyst. We assume a catalyst layer thickness of 1 nm in all cases. This may overestimate the amount of Pt required for HER catalysis, as recent research suggests that much lower Pt loading may be effective.³³

We assume the use of a TiO_2 protective layer to prevent corrosion of the photoelectrodes.^{34,35} In our base case we use a 60 nm thick TiO_2 layer, and we consider 30 nm and 120 nm thick layers in the low and high input cases, respectively. We assume the use of a 50 nm thick TCO layer made of fluorine doped tin oxide (FTO) in our base case, and a 10 nm thick FTO layer in our low energy input case. In our high input case, we consider a 100 nm thick layer of indium tin oxide (ITO) TCO, though this material may not be suitable if temperatures higher than 200 °C are needed in other fabrication processes.

We include the substrate for the thin film assembly as an active material because the electrical charge is transported through it. We consider a substrate of stainless steel, upon which the thin film layers are deposited. We select stainless steel because it is electrically conductive, flexible and resilient enough for use in roll-to-roll processing, and generally chemically resistant to acidic and basic environments. Different types of stainless steel are more resistant to acidic or basic conditions, so an appropriate type must be selected depending on the electrolyte solution. A 0.1 mm thick substrate is used in our base case. We consider a 0.2 mm thick substrate in our high energy input case, and a 0.05 mm thick substrate in our low energy input case.

Membranes of the PEC devices must be impermeable to the produced hydrogen and oxygen, and conductive to cations or anions. The most commonly used cation membrane material is perfluoro-sulfonic acid (PFSA), available commercially as Nafion®.³⁶ The required thickness of PFSA membrane depends on the device design and is assumed to total 50 μm for our base case. Our high energy input case assumes a 70 μm thick membrane, while our low energy input case uses a 30 μm thick membrane. Based on Zhai et al.¹⁰, the primary energy requirement for supplying raw materials for PFSA membrane production is estimated at 140 MJ per m^2 of membrane. Due to the geometry of the louvered device (Figure 2), which is established based on computational modelling for optimized ionic transport in electrolyte¹⁷, the membrane area is equal to 8.8% of the cell area, resulting in an energy use for membrane raw materials of 12 MJ per m^2 of cell area.

We consider the use of 1M H_2SO_4 solution as electrolyte, though we note that some of the electrode and catalyst materials would not be stable in an acidic environment. Alternatively, an electrolyte such as KOH

could be used to create a basic environment. Production of 1 kg of KOH requires over 10 times as much energy as production of 1 kg of H₂SO₄. However, this would have little impact on overall net energy, because 1 M H₂SO₄ electrolyte is responsible for only 0.07% of the total energy use for initial production of the facility. If 1 M KOH were used instead, this amount would increase to 0.7% of total initial energy use.

2.2.2. Embodied energy of inactive module materials

This category includes energy used for extraction, processing, and transportation to the cell factory gate of materials that are not active in the solar energy to fuel conversion process but are nevertheless essential to the performance of the device. These module materials include the transparent front cover, back cover, perimeter frame, and cell support ribs.

A module is 1 m wide and 1.2 m high, and is encapsulated on front and back by 2 mm thick float glass panes. We select glass as the encapsulation material due to its rigidity, transparency (a requirement only for the side facing the sun), resistance to harsh chemical environment, and relatively low embodied energy compared to metals or plastics. Properties of six potential encapsulation materials are detailed in Table S2 of the Supplementary Information, and additional information on glass properties and material selection criteria is in Section S3 of the Supplementary Information. We consider glass thicknesses of 3mm and 1mm in a sensitivity analysis. Use of 1 mm glass in the low case may be possible, because the glass is not freestanding but is adhered to periodic ribbed supports that reduce maximum span length and make the entire module a discrete structural element with glass skin and PVC webs.

For configurations that need to operate in basic electrolyte conditions, it will not be possible to use glass in direct contact with the electrolyte because the glass will etch over time. The glass may be protected by a thin polymer coating that is resistant to strong base, such as polyvinyl chloride, polypropylene, or ethylene-propylene diene monomer (EPDM).³⁷ The embodied energy of a 0.1 mm thick polypropylene layer is about 7 MJ/m². For comparison, the embodied energy of a 2 mm glass pane is 64 MJ/m². Covers of polycarbonate and poly(methyl methacrylate) may be used instead of glass, although their embodied energy is significantly higher: respectively about 260 MJ/m² and 340 MJ/m² for 2 mm thickness (see also Table S2).

A molded PVC perimeter frame surrounds the module, securing the glass panes and containing the electrolyte solution. We consider 3 alternative designs for the perimeter frame with low, medium (base case), and high material inputs (detailed in Supporting Information S4). A molded PVC ribbed framework supports the membrane and the thin-film substrate, and is adhered to the two glass panes (see Figure 2). We do not conduct modeling of oxygen gas flows, but assume the generated O_2 is simply vented. This requires further consideration, as a pressure difference between anodic and cathodic chambers may raise structural issues if O_2 is released uncontrolled. To avoid this, valves may be needed to ensure O_2 is released at a rate commensurate with H_2 evolution. There could be advantages to collecting and using the O_2 produced from water splitting, rather than considering it as a waste product to be disposed of. The embodied energy of O_2 collected from a large-scale PEC system was estimated at less than one-fifth that of O_2 derived from conventional separation processes.¹¹ The O_2 could be used as an input to other low-carbon energy systems, e.g. oxy-fuel CO_2 capture technology, thus employing industrial symbiosis to improve overall performance.

Our modeling assumes a generic 10% solar transmittance loss due to absorption, scattering and reflection, but does not specifically consider reflection from the glass surface. An anti-reflective (AR) coating may be applied to the surface of the glass cover, to reduce reflection loss that may be significant. A typical AR coating is MgF_2 , which is often deposited using vacuum evaporation methods. As discussed below, such thin film deposition processes may be energy intensive, thus the energy inputs for applying an AR coating should be weighed against the increased capture of solar energy. As an illustrative example, if we assume that an AR coating reduces reflective losses by 4%, this corresponds to about 340 MJ of increased hydrogen produced by a m^2 of cell during a 10-year life span with 10% STH efficiency. As this is roughly the same magnitude as the energy needed for thin film deposition (see Section 2.2.3), the net energy benefit of a conventional AR coating is questionable, and is not considered further. Reducing the energy intensity of thin film deposition processes, as discussed in the next section, may make AR coatings more favorable.

2.2.3. Energy intensity of active cell material fabrication

This category includes energy use for thin-film deposition of active cell materials, as well as for membrane fabrication. Data for manufacturing of thin film photovoltaics offer the most relevant information since the processes used are expected to be applicable to solar fuels technologies, although the materials sets are somewhat different. A variety of thin film deposition techniques are available,

including physical vapor deposition (PVD) methods³⁸ such as evaporation, sputtering, laser ablation, and arc-based emission; chemical vapor deposition (CVD) methods³⁹ such as thermal, plasma enhanced CVD, combustion CVD, and atomic layer deposition; and solution-based methods^{40,41} such as spin-coating, inkjet printing, spray pyrolysis, and gravure printing. These thin film deposition techniques may use energy for various purposes, e.g. vacuum, ion generation, heating, and cooling, which result in a wide range of process energy intensities.⁴² Process energy use may vary depending on pressure (high vacuum vs. low vacuum vs. atmospheric pressure) and required pumping speed, temperature (1000 °C range vs. 100 °C range vs. room temperature), film thickness (which directly correlates with processing time), precursor or source material (gas vs. solid), and other parameters. Economies of scale are seen in deposition energy use, with larger facilities using much less energy per square meter of deposited area.⁴³ This places constraints on how useful energy intensity data can be acquired for various processes. For example, theoretical values of energy use for vacuum pumping can be calculated for a single evacuation event. At industrial scale, however, load locks and transfer chambers are used instead of repeated venting-evacuation cycles, and efficiencies are gained by use of differential vacuum pumping of relatively small volumes for short times.⁴⁴ The geographic location of a manufacturing plant may also affect the energy intensities of production.⁴⁵

In our base case we assume the use of a state-of-the-art integrated inline coater, where multiple layers are deposited sequentially in the same vacuum chamber, thus minimizing the total energy use for vacuum pumping. Reviews of LCA studies of thin-film PV technologies^{30,46} show that direct process energy for thin-film deposition (of e.g. a-Si and CdTe PV modules) ranges from a low of 130 MJ/m² to a high of 1150 MJ/m², with most examples being in the range of 300-500 MJ/m². Although the use of PV manufacturing as a model for photoelectrochemical device fabrication does not fully capture likely processes, it is valuable for providing an initial process energy estimate. We select 400 MJ/m² as our base-case value for thin-film deposition energy, representing current best practice in an integrated inline deposition process. As a higher energy input case, we select 800 MJ/m² representing current average practice, which may involve non-integrated processes using separate sequential deposition lines. As a lower energy case, we consider a room temperature, atmospheric pressure, solution-based deposition method. A recent LCA of solution-processed perovskite solar modules⁴⁷ shows primary energy use for thin-film fabrication as low as 60 MJ/m², which we adopt as our low energy input case. Our low input case considers the use of amorphous Si electrodes made with a solution phase process, which is currently at an early stage of development and has not been deployed into manufacturing.⁴⁸ As currently practiced, it requires strictly water and air-free chemical handling and process conditions that will increase the

complexity and energy intensity of the method. We consider nevertheless the scenario, to determine the bounds of potential system benefits from technological improvements.

Energy is used for both material supply and fabrication of the membrane; material supply was discussed in Section 2.2.1. Based on Zhai et al.¹⁰, the primary energy requirement for fabrication of PFSA membrane is estimated to be 166 MJ per m² of membrane. Due to the geometry of the louvered device (Figure 2) the membrane area is equal to 8.8% of the cell area, resulting in an energy use for membrane raw materials of 15 MJ per m² of cell area.

2.2.4. Energy intensity of module assembly

This category includes encapsulation steps (e.g. cutting, pressing), other ancillary supplies (e.g. miscellaneous process chemicals), and indirect industrial processes (e.g. environmental control of manufacturing facilities such as space heating, cooling, ventilation, and air filtration). Based on Zhai et al.¹⁰, we assume a base-case value for module assembly of 241 MJ per m² of cell area. This parameter is subject to considerable uncertainty, and literature on energy use for large-scale PEC cell assembly is absent. We therefore assume a broad range of values in a sensitivity analysis, varying this parameter between 50% and 200% of base-case value.

2.3 Balance-of-system (BOS)

The net energy balance of PEC H₂ production is determined not only by the cell and module components such as photoelectrodes, catalysts, and encapsulation, but also by the BOS requirements such as structural supports, manifolds and pipes, pumps, compressors, storage tanks, pipelines, roads and monitoring systems. The modelled BOS characteristics are briefly described below, and elaborated in more detail by Sathre et al.¹¹ As discussed above, the modeled 1 GW hydrogen production facility is configured on five hierarchical levels: cells, modules, panels, fields, and facility. The two smallest levels, the cell and module, were described above in Section 2.2. The remaining three levels comprise the BOS (Figure 3). A total of 24 individual modules are mounted onto a truck-transportable “panel” of ~29 m². A “field” contains 1000 panels in a fixed flat array format, plus gas compression and storage, occupying 120,000 m². Finally, the 1 GW (annual average) “facility” comprises 1600 fields occupying 190 km² in the base-case of 10% STH efficiency.

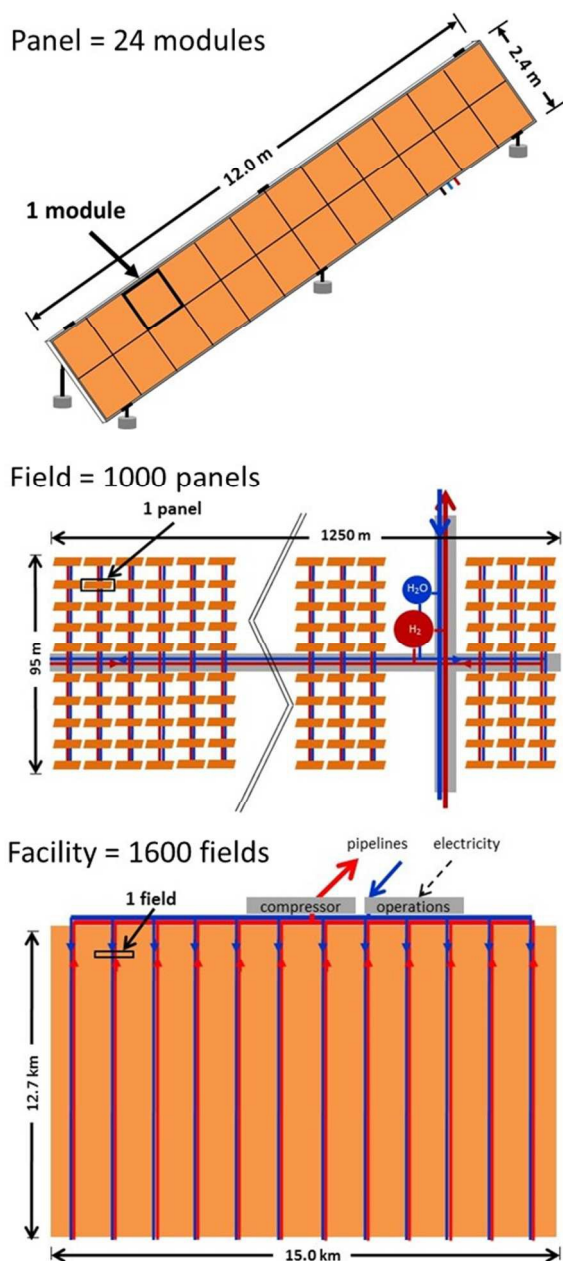


Figure 3. Three hierarchical levels (panel, field and facility) comprise the BOS of the 1 GW (continuous annual average) hydrogen production facility.

A “panel” is 12.0 m long by 2.4 m wide, and includes a structural frame upon which 24 PEC modules are mounted. Panels include onboard monitoring and diagnostics sensors, and pipe manifolds for transferring fluids to and from each module. Panels and modules have standardized fluid and data connections so they

can be installed and removed from the facility relatively easily to facilitate maintenance. The total weight of a complete panel is about 510 kg without electrolyte and 690 kg including electrolyte. The panels are fixed and are tilted towards the equator at an angle equal to the local latitude, here assumed to be 34° .

In the present study, our panel-level modeling differs in two ways from our previous work.¹¹ First, we have redesigned the panel structural elements to reduce the amount of steel required. The new design accommodates a lighter load (due mainly to thinner modules containing less electrolyte), and has a slightly more complex profile using two steel sections welded together rather than a single larger steel section. This reduces the amount of steel in each panel by 39%, from 340 kg to 207 kg. The panel structural design is described in Section S5 of the Supplementary Information. The second change in panel design is that the inactive area (percent of gross panel area that is not active solar collection area) is increased to 10%, from the 5% that we assumed in our previous analysis. This change is due to the supporting ribs in the louvered PEC modules (see Figure 2) that occupy surface area but do not capture solar energy, which were not present in the earlier microwire cell design. The active area is now 25.8 m^2 per panel. This change increases the number of panels needed to produce 1 GW of hydrogen, compared to the number calculated by Sathre et al.¹¹

A “field” comprises 1000 panels plus compression and storage infrastructure for one day’s production of H_2 . Spacing between panels is assumed to be 0.5 m end-to-end. Spacing between rows of panels is 9.5 m, based on a 10° shading angle. While the choice of size for a field is somewhat arbitrary, it represents an important organizational principle, that of distributed water supply, gas collection and compression, at a level intermediate between panel and facility levels, with all panels located within 50m of an access road for replacement with a mobile crane. In a final, optimized engineering design, there might be multiple levels of intermediate organization in a facility of this size, and the unit size could be considerably larger or smaller than the 1000 panels envisioned here. The field level is also envisioned to be of standardized spatial dimensions and therefore completely modular; an area of land at the facility level may have a complex topography and not occupy a simple rectangular area, but at the level of a field the installation could be completely regular and uniform.⁵

The entire “facility” aggregates production from 1600 fields, with a 90% capacity factor (i.e. on an average day 90% of the panels are producing H_2). Under base-case 10% STH efficiency, a total of 41.1 km^2 of active PEC solar collection area is needed, occupying 190 km^2 of land area. The facility is assumed to be located in the southwest US in an area of high insolation. Solar resource data are taken from NREL⁴⁹, and are the average of monthly mean flat-panel insolation at four sites: Phoenix, Daggett,

Tucson, and Las Vegas. The annual average solar insolation is 276 W/m^2 . In a sensitivity analysis, we also consider insolation data from a more representative selection of US sites: Charlotte, Omaha, Salt Lake City and Chicago. Details on solar insolation at each site are in section S6 of the Supplemental Information. We assume a life-span of 40 years for the facility. At the end of its service life, the facility will require decommissioning. This entails removing or remediating the infrastructure and equipment comprising the facility, and its safe disposal or recycling. Following the method used in the series of energy system life cycle assessments summarized by NETL⁵⁰, we assume that decommissioning requires 10% of the energy used for initial construction of the facility (here we consider only the energy used for BOS construction, because end of life management of cells and modules are discussed elsewhere). While in this study we analyze a large-scale 1GW facility, an interesting topic for future research is the suitability of smaller modular PEC facilities for deployment in the manner that PV is installed at smaller and variable scales.⁵¹

To determine the high input and low energy input values of the two BOS characteristics (Table 1), we conducted Monte Carlo simulations to estimate uncertainty introduced by interactions between multiple individual parameters describing the BOS. Simulation was conducted using Oracle® Crystal Ball software. Triangular probability distributions were assumed for each parameter based on low, base-case and high values (Table S3). Based on the outcome distribution of 10,000 simulations with simultaneous variation of each variable, the mean values of initial and ongoing BOS energy inputs are used as base-case parameter values, and 90% confidence intervals are used as high input and low input parameter values. Because the BOS requirements of a fixed-output facility will depend on STH efficiency and cell life span, we conducted nine separate simulations considering each combination of these parameters. Outcomes of the Monte Carlo simulations are shown in Figure S7 of the Supplementary Information.

3. Results and discussion

Table 2 shows the energy inputs for materials and fabrication of the cells and modules. In our base case, a total of 981 MJ primary energy will be needed to produce modules with 1 m^2 of active cell area. This energy input rises to 1843 MJ in our high input case, and drops to 373 MJ in our low input case. Fabrication of active cell components is the largest single energy input in the base case, mainly due to thin film deposition process energy. Energy use for both materials and fabrication of inactive module components are the next biggest inputs. Energy use for supplying active cell materials is the least significant input. There is a tenfold range in energy use for active cell fabrication, from $\sim 70 \text{ MJ/m}^2$ in the

low energy input case, to over 800 MJ/m² in the high energy case. Progress in reducing the energy intensity of thin film deposition processes is an opportunity to improve net energy performance.

Table 2. Summary of high input, base case, and low input values of energy use for PEC cell and module production (MJ primary energy per m² active cell area).

	High energy input	Base case	Low energy input
Active cell materials	194.3	93.3	40.6
<i>Thin-film materials</i>	53.9	18.1	0.8
<i>Membrane materials</i>	15.6	12.2	7.6
<i>Conductive substrate</i>	123.4	61.7	30.9
<i>Electrolyte</i>	1.4	1.4	1.4
Inactive module materials	348.5	231.8	143.0
<i>Glass window*</i>	106.2	70.8	35.4
<i>Glass back cover*</i>	106.2	70.8	35.4
<i>Supporting ribs</i>	51.5	51.5	51.5
<i>Perimeter frame</i>	84.7	38.7	20.8
Active cell fabrication	818.6	414.5	69.1
<i>Thin-film deposition</i>	800.0	400.0	60.0
<i>Membrane fabrication</i>	18.6	14.5	9.1
Inactive module fabrication	481.9	240.9	120.5
Total without BOS	1843	981	373

* The embodied energy values for glass shown here are greater than those discussed in Section 2.2.2 and listed in Table S2, because these values are expressed per m² of active cell area. Active cell area is 90% of total module area.

We observe that several of the materials considered here as raw materials for cell or module production (e.g. stainless steel, glass, PVC) are all the finished products of earlier production processes, which each required their own raw materials. Thus, the energy use breakdown begun in Table 2 could further distinguish the embodied energy of these materials, e.g. energy used for mineral extraction, ore processing, transport, and refining. For example, a typical soda-lime glass composition used for window glass consists of ~60% silica sand, ~20% sodium monoxide derived from soda ash (sodium carbonate), and ~18% calcium monoxide derived from limestone (calcium carbonate).⁵² The raw materials (sand, limestone and soda ash) are combined and heated, typically using methane fuel. The melted glass is formed into sheets on a float bed, and cooled until solid. The glass sheets are then cut to size and annealed. Heating the raw materials to melting temperature is the most energy-intensive process step in glass production in continuous furnaces, contributing over half of the embodied energy of the finished

product. Supply of raw materials (silica sand, limestone, soda ash) including extraction, primary processing and transport, contributes less than 15% of the embodied energy (authors' calculation based on ^{52,53}). Another example is stainless steel production. There are numerous grades of stainless steel that are produced, the most common being 18-8 type comprised of 74% Fe, 18% Cr and 8% Ni. Each of these metals is obtained from ores of various composition. Energy use for mining, beneficiating and transporting the metal ores contributes only about 8% of the total embodied energy of stainless steel.⁵⁴ Most of the embodied energy is due to high temperature thermochemical refining processes.

A breakdown of the embodied energy of the precursor materials used for thin film layers is shown in Table 3. The variations between the high energy input case, base case, and low energy input case are due to different selection of materials, different layer thicknesses, and different values for the material utilization efficiency and the ratio of embodied energy of the refined element to that of the precursor materials. The totals in Table 3 are included in Table 2 under the heading "Thin film materials". Details on these materials and various other materials used in thin films are in Section S1 of the Supplementary Information. Comparison to Table 2 shows that energy use for supplying active cell materials is a minor part of total life cycle energy use.

Table 3. Embodied energy of precursor materials to the thin film layers, for the high input, base case, and low input cases (MJ primary energy per m² active cell area).

Thin film layer	High energy input	Base case	Low energy input
OER catalyst	5.8	2.9	0.001
Protective layer	2.4	0.60	0.15
Photoanode	8.2	1.1	0.56
TCO	5.5	0.17	0.02
Photocathode	9.5	2.0	0.02
HER catalyst	22.6	11.3	<0.001
Total	53.9	18.1	0.75

Figure 4 compares the production energy use of the louvered thin-film cell design analyzed here to the silicon microwire cell design studied by Zhai et al.¹⁰ The louvered thin-film cell design uses substantially less energy for production (base-case value of 981 MJ/m²) than the silicon microwire design (base-case value of 2110 MJ/m²). Major improvements are due to reduced energy for fabricating photoactive

components, and reduced embodied energy of inactive materials. This demonstrates that innovative cell design and manufacture can improve net energy performance.

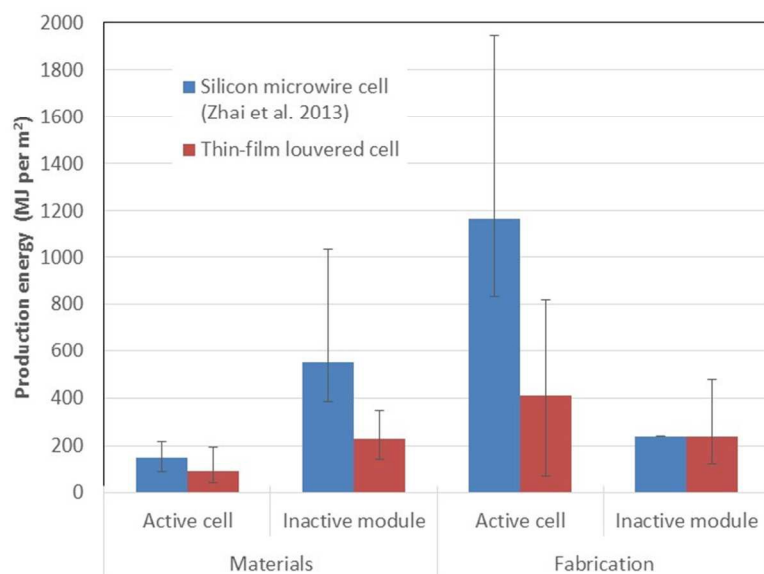


Figure 4. Production energy use for louvered thin-film cell design is substantially lower than that estimated by Zhai et al.¹⁰ for a silicon microwire cell design.

Figure 5 shows the energy inputs for initial BOS production and for ongoing BOS operation and EOL, under different STH efficiencies and with low, base and high energy inputs. These BOS energy use values are based on the Monte Carlo simulation results detailed in section S7 of the Supplemental Information, and are normalized to annual energy use. The ongoing energy inputs, mainly for BOS operation but also including EOL, are found to be substantially greater than the initial energy inputs for BOS production.

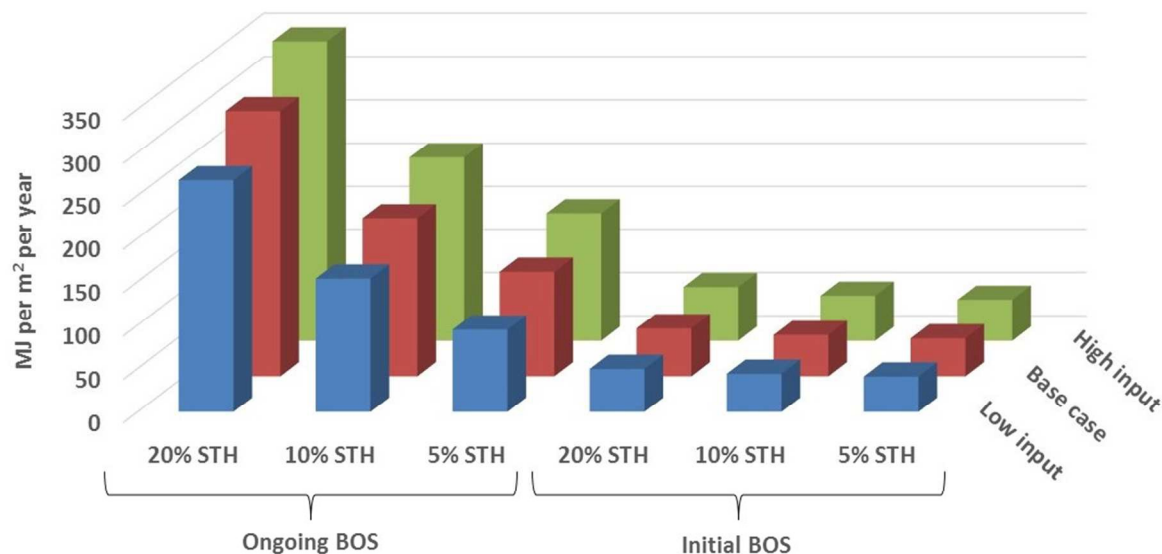


Figure 5. Energy use for initial and ongoing BOS, under different conditions of STH efficiency and with high input, base case, and low input parameter values (MJ primary energy per m² active cell area per year).

Figure 6 shows the annual energy balance of the H₂ production facility in operation, under base-case conditions at 10% STH efficiency. The energy content of the H₂ produced corresponds to 31.5 PJ of primary energy per year, which is equivalent to 1 GW continuous power for one year. From this positive value is subtracted the primary energy needed to operate the production system. The largest single energy use is for gas compression, which uses 5.0 PJ of primary energy per year. It may be possible to reduce this compression energy need by designing cells to produce H₂ at higher pressure, using an overpotential of 0.06 eV per atm to drive H₂ production at elevated pressure.⁵⁵ Maintaining cells and panels above atmospheric pressure would entail trade-offs between the decreased energy requirements for gas compression and the higher performance needs of other components including module encapsulation and pipes. Module replacement is the second largest energy input, using 4.1 PJ per year under steady-state conditions with a 10-year cell life span (i.e. 10% of all modules in the facility are replaced each year). Module replacement includes full material and fabrication energy for new cells and modules; material recycling is not explicitly considered. The energy for module replacement is less than half of the 8.7 PJ/year estimated in our previous work¹¹, due to the lower energy intensity of cell fabrication and the reduced module material use (Figure 4). Energy use for module replacement depends strongly on cell life span; error bars in Figure 6 show that 8.3 PJ/yr is needed with a 5-year life span, and only 2.1 PJ/yr is used with a 20-year cell life span. Module heating to avoid electrolyte freezing on cold winter nights was

estimated in our previous work to require 1.5 PJ per year.¹¹ The internal convection coefficients of the louvered design are different from the previous microwire system, resultant from the changes to the internal cell geometry, but we assume this will not significantly change the heating energy requirement. The need for module heating is discussed further in Section S8 of the Supplementary Information. Energy use for gas handling, water supply and facility operations is minor. In total, about 11.4 PJ of energy inputs are needed per year, resulting in a net energy delivery of 20.1 PJ of primary energy per year, under base-case conditions. In Figure 6, error bars for Module heating represent the coldest and warmest of four modeled locations, and for Gas compression, Gas handling, Water supply and Facility operation are based on parameter sensitivity modeling. The error bars for Net energy delivered are the sums of the other error bars.

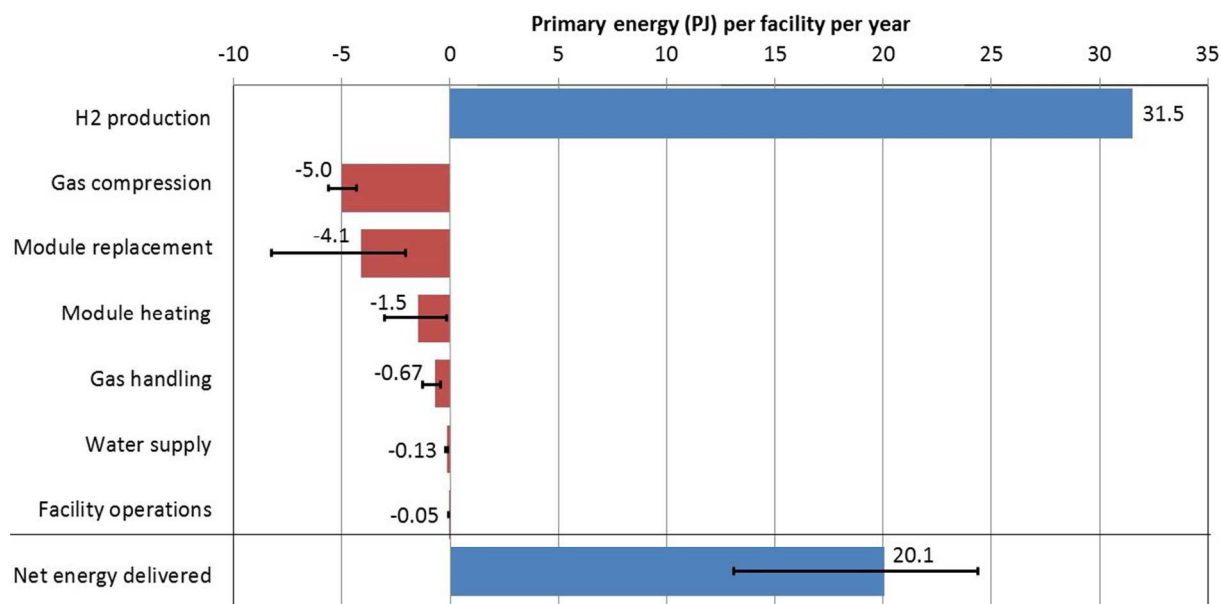


Figure 6. Annual energy balance (PJ year⁻¹) of 1 GW (annual average) H₂ production facility in operation under base-case conditions.

Figure 7 shows the one-time energy inputs required to produce and decommission the 1 GW H₂ facility. Under base-case conditions, initial construction will need a total of 72.9 PJ of primary energy. The energy use for materials and fabrication of cells and modules represents the energy investment to initially equip the complete facility with PEC cells and modules; thereafter, energy use for periodic replacement of the cells and modules is accounted for in the annual energy balance (Figure 6). The estimated energy input

for decommissioning of the facility at the end of its service life is 3.4 PJ. These one-time inputs are compared to the annual delivered energy of the facility in operation (from Figure 6), shown as a dashed line. Under base case conditions, it will take about 4.1 years of operation to deliver energy that is equivalent to that used for initial construction and final decommissioning. Over the 40-year projected service life of the facility, the EROEI is 2.34 and the life cycle primary energy balance is +720 PJ. This net energy performance is substantially better than that estimated in our previous analysis of silicon microwire cell design.¹¹ The current energy payback time is half of the 8.1 years estimated previously, the EROEI is 29% higher than the previous estimate of 1.66, and the current energy balance is 31% higher than the +500 PJ estimated by Sathre et al.¹¹ The improved net energy performance is largely due to the reduced energy inputs for cell and module production, which results in lower initial energy use for facility construction (Figure 7), as well as lower ongoing energy use for cell replacement (Figure 6).

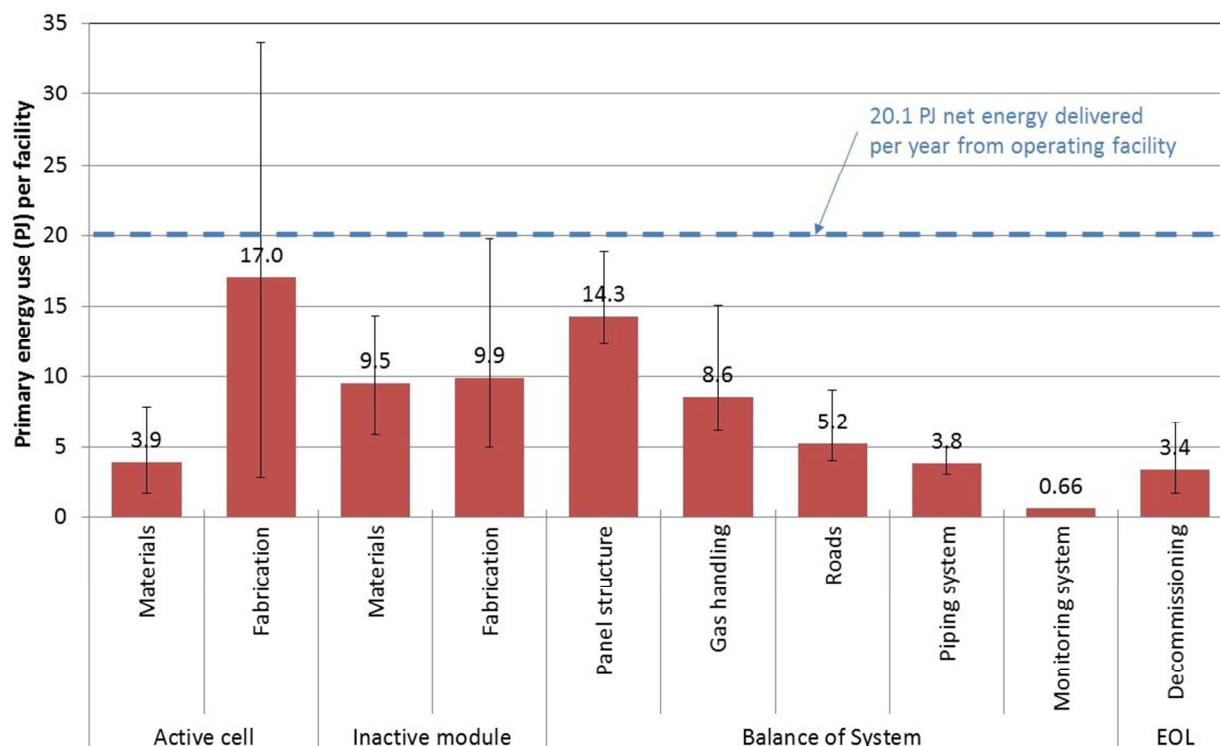


Figure 7. One-time primary energy inputs (PJ) required to construct and decommission a 1 GW (annual average) facility. For comparison, the base-case annual delivered energy of the completed facility in operation is shown as a blue dashed line.

Figure 8 shows the change in the three net energy metrics (life cycle energy balance, EROEI, energy payback time) due to one-at-a-time variation of eight individual parameters between their low and high

values. Two of the parameters describe the embodied energy of cell and module materials, two describe the energy intensity of cell and module fabrication processes, two describe the initial and ongoing energy use of the BOS, and two parameters describe cell performance (STH efficiency and cell life span). STH efficiency is overwhelmingly the parameter variation causing the most significant change in all three metrics. Current prototype cells typically range from 5% to 10% STH efficiency, with 20% being an aspirational upper limit. Variation of PEC cell life span is the second most significant parameter. The range of energy use for active cell fabrication, dominated by thin-film deposition energy use, is the third most significant parameter. Variation in ongoing energy use for BOS operation is the next most significant. The modeled range of variation is much less significant for other parameters, including inactive module materials and fabrication, active cell materials, and initial BOS energy use. We also observe the importance of solar insolation levels, which are a function of location. Using insolation data from north-central US locations instead of the base-case southwest US locations, the EROEI is reduced from 2.34 to 1.74, and the energy payback time is increased from 4.1 years to 6.8 years (not shown in Figure 8).

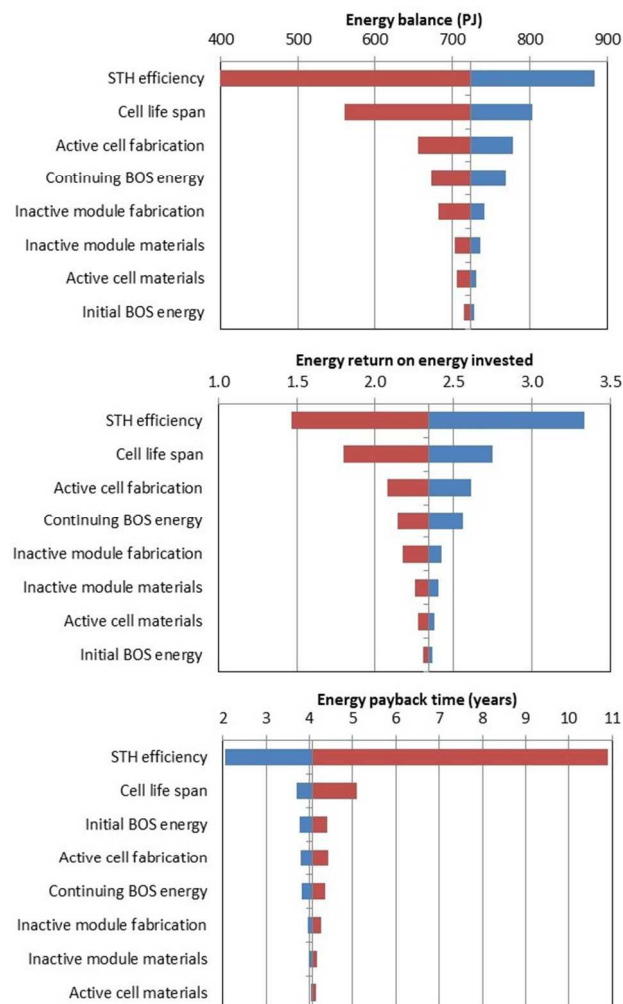


Figure 8. Effect on system performance metrics of individual variation of key parameters from their base-case values. Top image shows energy balance; middle image shows EROEI; bottom image shows energy payback time. Blue bars indicate improved net energy performance compared to base-case, while red bars indicate reduced net energy performance.

We examined the question of whether more efficient and longer lived devices that require higher energy inputs for materials or fabrication will exhibit improved net energy performance, compared to less efficient and shorter lived devices with lower energy input. To explore these relations, we compare three PEC systems, with all six characteristics (from Table 2) at the low input, base case, and high input values, respectively. Furthermore, we assume that the system with low inputs performs at 5% STH efficiency and 5-year life span, the base case system performs at 10% STH efficiency and 10-year life span, and the high

input system performs at 20% STH efficiency and 20-year life span. We emphasize that such quantitative relations are purely illustrative, and are based neither on laboratory experience nor theoretical computation. Nevertheless, given the plausible ranges we consider of energy inputs, STH efficiency and life span, such exploratory analysis can provide insight into broad trends and sensitivities. Figure 9 shows that under the modeled conditions, the high input system gives much better overall energy performance. The low input system, despite lower energy inputs than the other systems, delivers reduced life cycle net energy due to its lower hydrogen production rate and shorter life span. This suggests that high STH efficiency and long life spans are primary design requirements for PEC systems, even if such performance requires additional energy and material inputs for production and operation.

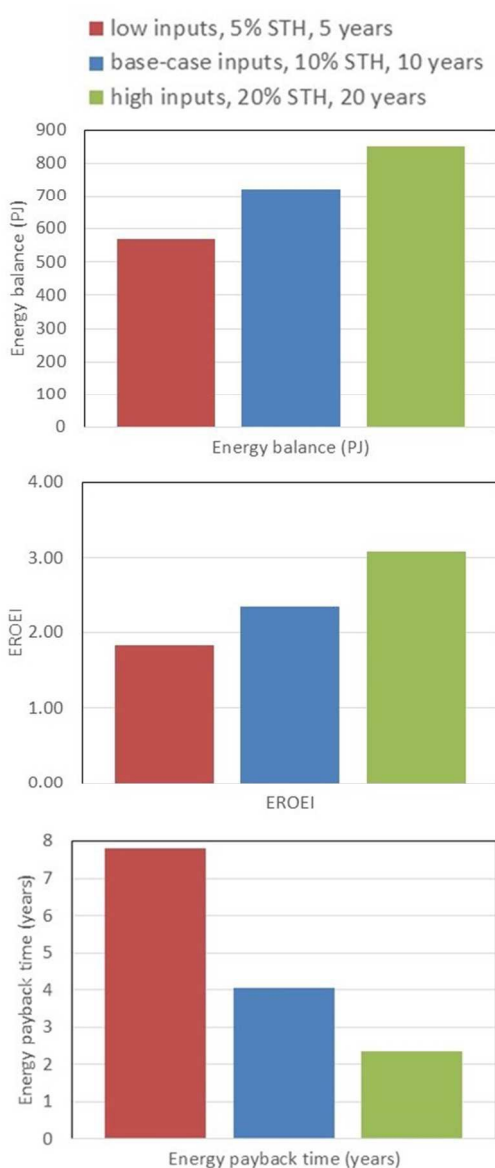


Figure 9. System performance metrics of 3 combinations of parameters: low input and low performance (left bars), base case inputs and base case performance (middle bars), and high input and high performance (right bars).

Our model already assumes re-use of panel support structure, manifold pipes, and sensors upon replacement of PEC modules. If inactive module materials (glass window, glass back cover, PVC support ribs and PVC frame) are also re-used at the end of cell life span, the system performance improves because less energy is required to produce replacement cell materials. The energy balance increases by 5% to +760 PJ, the energy return on energy invested increases 8% to 2.5, and the energy pay-back time decreases by 5% to 3.9 years. The suitability of re-use of glass encapsulation materials may be limited by the possible damage to the glass after years of use, e.g. by etching by wind-blown sand. While there are clear energy benefits of direct re-use of glass products (e.g. glass containers), the energy benefits are much less if the recovered glass must be melted and reconfigured.⁵³

We also conduct a scale-up analysis to estimate required quantities of thin film materials and identify potential constraints in material availability. We consider three hydrogen demand scale-up scenarios of varying extent, which are detailed in Section S9 of the Supplemental Information. The lowest demand scenario assumes that 10% of US light-duty vehicle demand in 2040 would be satisfied by hydrogen from our modeled facilities. This amount of scale-up is expected to require 14 facilities producing 1 GW (continuous annual average) each. The middle scenario assumes 100% of US light-duty vehicle demand in 2040 would be satisfied by facility-generated hydrogen, and would require 142 1 GW facilities. The highest demand scenario assumes that 100% of global light-duty vehicle demand in 2040 would be satisfied by facility-generated hydrogen, and is projected to require 850 facilities of 1 GW each. We calculate the amount of thin film materials that would be required annually for these hydrogen production facilities, assuming an STH efficiency of 10%, a cell life span of 10 years, and a material utilization efficiency of 50%. We compare the annual scenario requirement for each element to the 2014 global primary mine production of each element⁵⁶, as an initial estimate of scale-up feasibility.

For many of the thin film materials, particularly the abundant materials such as Si, Fe, Ni, Cu, P, Sn, Ti and V, large-scale deployment of PEC hydrogen generation would require a very low proportion of current global mine production, suggesting that supply constraints are unlikely. At the lowest scale-up level (10% of US demand by 2040), only tellurium (as part of CdTe photoelectrode) and iridium (as OER catalyst) show likely supply constraints, each requiring over 30% of current production rates of the

elements. If scaled-up to meet 100% of US demand by 2040, gallium (as part of GaAs or InGaP photoelectrodes) and indium (a component of InP and InGaP photoelectrodes as well as ITO TCO layers) begin to show likely supply constraints. At the 2040 global scale-up level, platinum (as HER catalyst) and bismuth (as part of BiVO₄ photoelectrode) supply would likely be constrained, and the quantities of Te, Ir, In and Ga required annually would exceed current primary production rates of these elements. We note, however, that we may significantly overestimate the amount of Pt needed for HER catalysis, as indicated by recent research.³³ Results of the scale-up material use analysis are detailed in Section S9 of the Supplemental Information. An important caveat when comparing against current mine production is that future production may differ substantially due to changes in economic demand or extraction and processing technology. Resource constraints for key materials may be encountered due to limited absolute quantities of materials, or to conflicts with other potential uses of the materials. Some industrially important elements such as In, Bi, Co, Ga and Cd are extracted as by-products of other mining processes, thus have low price-elasticity of supply.⁵⁷ Potential material constraints are yet to be fully incorporated into most technology assessments. The LCA framework traditionally includes a “resource depletion” impact category, though the longer time scale and non-linear response of that impact compared to some other categories makes objective comparison difficult. The emerging metric of “material criticality” takes into account two aspects: the risks to reliable supply of a material, and vulnerability of a technological system to a potential supply disruption of the material.⁵⁸

4. Conclusions

We have used prospective life cycle assessment, an approach to provide early insight on emerging technologies, to understand the potential net energy implications of eventual large-scale manufacturing, deployment, and operation of a PEC hydrogen production system. We measured three indices of net energy performance (life cycle primary energy balance, energy return on energy invested, and energy payback time), as indicators of system-wide energetic viability of the technology.

This prospective LCA has identified several priorities for PEC development efforts. First, the STH conversion efficiency of cells has a very strong impact on net energy viability of a PEC H₂ system. STH efficiency remains a primary system requirement. Our modeling suggests that STH efficiency well above 5% is needed for net energy viability. Second, the cell life span also has strong net energy significance; a cell with life span less than five years will be energetically challenged. The third most important

parameter is the energy intensity of cell fabrication, where low-energy thin film deposition processes will improve performance. The other system characteristics are less important, including inactive module fabrication, active cell materials, inactive module materials, and BOS energy use. Facility location is important, and high-insolation sites should be selected for improved net energy. STH efficiency and cell life span remain the predominant source of system-wide variability and uncertainty regarding PEC net energy performance. This suggests that a marginal increase in energy use for cell production will be energetically rewarded to the extent it increases STH efficiency or cell life span.

This work has demonstrated that innovative design and manufacture can improve the net energy performance of PEC systems, and could be expanded to include concentrating PEC devices (e.g.⁵⁹). Concentration may improve net energy performance because of the potentially higher STH efficiency and the use of a smaller active collection area, as has been suggested in an analysis of a PV-electrolyzer system for H₂ generation.⁶⁰ However, concentration mechanisms require more inactive materials, e.g. for tracking and optics. A detailed net energy analysis could elucidate these trade-offs. The analytical framework could be further improved by quantitatively linking cell production energy with cell performance. Increasing availability of material characterization data⁶¹ should allow robust performance-based analysis of a wide range of potential configurations.⁶²

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References

- 1 S. Chu and A. Majumdar, Opportunities and challenges for a sustainable energy future, *Nature*, 2012, **488**, 294–303.
- 2 International Energy Agency (IEA), *Key World Energy Statistics*, Paris, 2014.

- 3 Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2013: The Physical Science Basis*, Working Group I Contribution to the Fifth IPCC Assessment Report, 2013. Web-accessed at <https://www.ipcc.ch/report/ar5/wg1/>
- 4 National Academy of Sciences (NAS), *Hidden Costs of Energy: Unpriced Consequences of Energy Production and Use*, Washington DC, 2010. Web-accessed at http://www.nap.edu/catalog.php?record_id=12794
- 5 S. Ong, C. Campbell, P. Denholm, R. Margolis and G. Heath, *Land-Use Requirements for Solar Power Plants in the United States*, National Renewable Energy Laboratory, Report NREL/TP-6A20-56290, 2013.
- 6 N. Espinosa, M. Hosel, D. Angmo and FC Krebs, Solar cells with one-day energy payback for the factories of the future, *Energy Environ. Sci.*, 2012, **5**, 5117-5132.
- 7 Z. B. Chen, T.F. Jaramillo, T.G. Deutsch, A. Kleiman-Shwarscstein, A.J. Forman, N. Gaillard, R. Garland, K. Takanebe, C. Heske, M. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner and H.N. Dinh, Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols, *Journal of Materials Research*, 2010, **25**, 3-16.
- 8 J. Rongé, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordiga and J.A. Martens, Monolithic cells for solar fuels, *Chemical Society Reviews*, 2014, **43**, 7963–81.
- 9 J.W. Ager III, M. Shaner, K. Walczak, I.D. Sharp and S. Ardo, Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. *Energy Environ. Sci.*, 2015, **8**, 2811-2824.
- 10 P. Zhai, S. Haussener, J. Ager, R. Sathre, K. Walczak, J. Greenblatt and T. McKone, Net primary energy balance of a solar-driven photo-electrochemical water-splitting device, *Energy Environ. Sci.*, 2013, **6**, 2380-2389.
- 11 R. Sathre, C.D. Scown, W.R. Morrow, J.C. Stevens, I.D. Sharp, J.W. Ager, K. Walczak, F.A. Houle and J.B. Greenblatt, Life-cycle net energy assessment of large-scale hydrogen production via photoelectrochemical water splitting, *Energy Environ. Sci.*, 2014, **7**: 3264-3278.
- 12 B.A. Pinaud, J.D. Benck, L.C. Seitz, A.J. Forman, Z. Chen, T.G. Deutsch, B.D. James, K.N. Baum, G.N. Baum, S. Ardo, H. Wang, E. Miller and T.F. Jaramillo, Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry, *Energy Environ. Sci.*, 2013, **6**, 1983.
- 13 A.C. Nielander, M.R. Shaner, K.M. Papadantonakis, S.A. Francis and N.S. Lewis, A taxonomy for solar fuels generators, *Energy Environ. Sci.*, 2015, **8**, 16–25.

- 14 G. Peharz, F. Dimroth and U. Wittstadt, Solar hydrogen production by water splitting with a conversion efficiency of 18%, *International Journal of Hydrogen Energy*, 2007, **32**, 3248-3252.
- 15 A. Fujishima and K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature*, 1972, **238**, 37-38.
- 16 S.Y. Reece, J.A. Hamel, K. Sung, T.D. Jarvi, A.J. Esswein, J.J.H. Pijpers, D.G. Nocera, Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts, *Science*, 2011, **334**, 645-648.
- 17 K. Walczak, Y. Chen, C. Karp, J.W. Beeman, M. Shaner, J. Spurgeon, I.D. Sharp, X. Amashukeli, W. West, J. Jin, N. Lewis and C. Xiang, Modeling, simulation, and fabrication of a fully integrated, acid-stable, scalable solar-driven water-splitting system, *ChemSusChem*, 2015, **8**, 544-551.
- 18 M.R. Shaner, J.R. McKone, H.B. Gray and N.S. Lewis, Functional integration of Ni–Mo electrocatalysts with Si microwire array photocathodes to simultaneously achieve high fill factors and light-limited photocurrent densities for solar-driven hydrogen evolution. *Energy Environ. Sci.*, 2015, **8**, 2977-2984.
- 19 C. Xiang, Y. Chen and N.S. Lewis, Modeling an integrated photoelectrolysis system sustained by water vapor, *Energy Environ. Sci.*, 2013, **6**, 3713-3721.
- 20 M. Modestino, M. Dumortier, S. Hashemi, S. Haussener, C. Moser and D. Psaltis, Vapor-fed microfluidic hydrogen generator, *Lab on a Chip*, 2015, **15**, 2287-2296.
- 21 M.R. Singh, E.L. Clark and A.T. Bell, Effects of electrolyte, catalyst, and membrane composition and operating conditions on the performance of solar-driven electrochemical reduction of carbon dioxide, *Phys.Chem.Chem.Phys.*, 2015, **17**, 18924.
- 22 M. Schreier, L. Curvat, F. Giordano, L. Steier, A. Abate, S.M. Zakeeruddin, J. Luo, M.T. Mayer and M. Grätzel, Efficient photosynthesis of carbon monoxide from CO₂ using perovskite photovoltaics, *Nat. Commun.*, 2015, **6**, 7326.
- 23 T. Arai, S. Sato and T. Morikawa, A monolithic device for CO₂ photoreduction to generate liquid organic substances in a single-compartment reactor, *Energy Environ. Sci.*, 2015, **8**, 1998–2002.
- 24 Ecoinvent, *Ecoinvent v2.2 Life Cycle Inventory (LCI) database*, 2012. Web-accessed at www.ecoinvent.org
- 25 P. Nuss and M.J. Eckelman, Life cycle assessment of metals: A scientific synthesis, *PLOS One*, 2014, **9**, e101298.
- 26 E. Williams, N. Krishnan and S. Boyd, Ultrapurity and energy use: Case study of semiconductor manufacturing, Chapter 7 in: B.R. Bakshi, T.G. Gutowski and D.P. Sekulic DP (eds.), *Thermodynamics and the Destruction of Resources*, Cambridge University Press, 2014.

- 27 H.-J. Althaus, M. Chudacoff, R. Hischer, N. Jungbluth, M. Osses and A. Primas, *Life Cycle Inventories of Chemicals*, Final report ecoinvent data v2.0 No. 8. Swiss Centre for Life Cycle Inventories, Dübendorf, Switzerland, 2007.
- 28 M.A. Kreiger, D.R. Shonnard and J.M. Pearce, Life cycle analysis of silane recycling in amorphous silicon-based solar photovoltaic manufacturing, *Resources, Conservation and Recycling*, 2013, **70**, 44-49.
- 29 V. Fthenakis, Sustainability of photovoltaics: The case for thin-film solar cells, *Renewable and Sustainable Energy Reviews*, 2009, **13**, 2746-2750.
- 30 E. Alsema, Energy requirements of thin-film solar cell modules: A review. *Renewable & Sustainable Energy Reviews*, 1998, **2**, 387-415.
- 31 K. Zweibel, Thin film PV manufacturing: Materials costs and their optimization, *Solar Energy Materials & Solar Cells*, 2000, **63**, 375-386.
- 32 C.L.C. McCrory, S. Jung, J.C. Peters and T.F. Jaramillo, Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction, *J. Am. Chem. Soc.*, 2013, **135**, 16977-16987.
- 33 E. Kemppainen, A. Bodin, B. Sebok, T. Pedersen, B. Seger, B. Mei, D. Bae, P. C. K. Vesborg, J. Halme, O. Hansen, P. D. Lund and I. Chorkendorff, Scalability and feasibility of photoelectrochemical H₂ evolution: the ultimate limit of Pt nanoparticle as an HER catalyst, *Energy Environ. Sci.*, 2015, **8**, 2991-2999.
- 34 B. Seger, T. Pedersen, A.B. Laursen, P.C.K. Vesborg, O. Hansen, and I. Chorkendorff, Using TiO₂ as a conductive protective layer for photocathodic H₂ evolution, *J. Am. Chem. Soc.*, 2013, **135**, 1057-1064.
- 35 S. Hu, M.R. Shaner, J.A. Beardslee, M. Lichterman, B.S. Brunschwig and N.S. Lewis, Amorphous TiO₂ coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation, *Science*, 2014, **344**, 1005-1009.
- 36 G. Hoogers (ed.), *Fuel Cell Technology Handbook*, CRC Press, Boca Raton, London, New York, Washington DC, 2003.
- 37 IPEX, *Chemical Resistance Guide: Thermoplastic Piping Systems*, 2001.
- 38 S.M. Rossnagel, Thin film deposition with physical vapor deposition and related technologies, *J. Vac. Sci. Technol. A*, 2003, **21**(5), S74-S87.
- 39 M.J. Hampden-Smith and T.T. Kodas, Chemical vapor deposition of metals: Part 1: An overview of CVD processes. *Chem. Vap. Deposition*, 1995, **1**, 8-23.
- 40 R.M. Pasquarelli, D.S. Ginley and R. O'Hayre, Solution processing of transparent conductors: From flask to film, *Chem. Soc. Rev.*, 2011, **40**, 5406-5441.

- 41 S.J. Kim, S. Yoon and H.J. Kim, Review of solution-processed oxide thin-film transistors, *Japanese Journal of Applied Physics*, 2014, **53**, 02BA02.
- 42 C.A. Wolden, J. Kurtin, J.B. Baxter, I. Repins, S.E. Shaheen, J.T. Torvik, A.A. Rockett, V.M. Fthenakis and E.S. Aydil, Photovoltaic manufacturing: Present status, future prospects, and research needs, *Journal of Vacuum Science and Technology A*, 2011, **29**, 030801.
- 43 A. Shah, J. Meier, A. Buechel, U. Kroll, J. Steinhauser, F. Meillaud, H. Schade and D. Domine, Towards very low-cost mass production of thin-film silicon photovoltaic (PV) solar modules on glass, *Thin Solid Films*, 2006, **502**, 292-299.
- 44 R.J. Hill and S.J. Nadel, *Coated Glass Applications and Markets*, BOC Coating Technology, Fairfield CA, 1999.
- 45 D. Yue, F. You S.B. Darling, Domestic and overseas manufacturing scenarios of silicon-based photovoltaics: Life cycle energy and environmental comparative analysis, *Solar Energy*, 2014, **105**, 669-678.
- 46 J. Peng, L. Lu and H. Yang, Review on life cycle assessment of energy payback and greenhouse gas emission of solar photovoltaic systems, *Renewable & Sustainable Energy Reviews*, 2013, **19**, 255-274.
- 47 J. Gong, S.B. Darling and F. You, Perovskite photovoltaics: Life-cycle assessment of energy and environmental impacts, *Energy Environ. Sci.*, 2015, **8**, 1953-1968.
- 48 T. Bronger, P.H. Wöbkenberg, J. Wördenweber, S. Muthmann, U.W. Paetzold, V. Smirnov, et al., Solution-based Silicon in thin film solar cells, *Advanced Energy Materials*, 2014, **4**, 1301871.
- 49 National Renewable Energy Laboratory (NREL), *PV-Watts calculator*, 2015. Web-accessed at <http://pvwatts.nrel.gov/index.php>
- 50 National Energy Technology Laboratory (NETL), *Life Cycle Analysis: Power Studies Compilation Report*, National Energy Technology Laboratory Report DOE/NETL-2010/1419, 2010.
- 51 E. Dahlgren, C. Gocmen, K. Lackner and G. van Ryzin, Small modular infrastructure, *The Engineering Economist*, 2013, **58**, 231-264.
- 52 E. Worrell, C. Galitsky, E. Masanet and W. Graus, *Energy Efficiency Improvement and Cost Saving Opportunities for the Glass Industry*, Report LBNL-57335, Lawrence Berkeley National Laboratory, 2008.
- 53 L.L. Gaines and M.M. Mintz, *Energy Implications of Glass-Container Recycling*, Report ANL/ESD-18, Argonne National Laboratory, 1994.
- 54 J. Johnson, B.K. Reck, T. Wang and T.E. Graedel, The energy benefit of stainless steel recycling, *Energy Policy*, 2008, **36**, 181-192.
- 55 J.S. Newman and K.E. Thomas-Alyea, *Electrochemical Systems*, Hoboken, N.J, J. Wiley, 2004.

- 56 United States Geological Survey (USGS), *Mineral Commodity Summaries*, 2015.
<http://minerals.usgs.gov/minerals/pubs/commodity/>
- 57 P.C.K. Vesborg and T.F. Jaramillo, Addressing the terawatt challenge: Scalability in the supply of chemical elements for renewable energy, *RSC Advances*, 2012, **2**, 7933-7947.
- 58 American Physical Society (APS) and Materials Research Society (MRS), *Energy Critical Elements: Securing Materials for Emerging Technologies*, 2011. <http://www.aps.org/policy/reports/popa-reports/upload/elementsreport.pdf>
- 59 Y. Chen, C. Xiang, S. Hu and N.S. Lewis, Modeling the performance of an integrated photoelectrolysis system with 10× solar concentrators. *Journal of the Electrochemical Society*, 2014, **161**, F1101-F1110.
- 60 M. Dumortier and S. Haussener, Design guidelines for concentrated photo-electrochemical water splitting devices based on energy and greenhouse gas yield ratios, *Energy Environ. Sci.*, 2015, **8**, 3069-3082.
- 61 C.C.L. McCrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters and T.F. Jaramillo, Benchmarking HER and OER electrocatalysts for solar water splitting devices. *J. Am. Chem. Soc.*, 2015, **137**, 4347-4357.
- 62 M. Dumortier, S. Tembhurne and S. Haussener, Holistic design guidelines for solar hydrogen production by photo-electrochemical routes. *Energy Environ. Sci.*, 2015, **8**, 3614-3628.

Broader Context

Long-term human development will require environmentally benign renewable energy supply systems, to replace our current dependence on fossil fuels. The net energy of such systems, i.e. the renewable energy harvested minus the energy used to build and operate the system, must be substantially positive to enable energetic benefits to society. Using prospective life cycle modeling, we assess the net energy balance of large-scale hydrogen fuel production via solar driven photoelectrochemical water splitting technology. We identify the factors that strongly improve net energy performance, including high solar-to-hydrogen conversion efficiency, long life span of the water splitting device, and low energy use for manufacturing the device. Solar fuels research should focus on achieving success in these factors, to enable future deployment of solar fuel systems that provide meaningful energy services to society.