

## ANALYSIS

## Net primary energy balance of a solar-driven photoelectrochemical water-splitting device

Cite this: *Energy Environ. Sci.*, 2013, **6**, 2380

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A fundamental requirement for a renewable energy generation technology is that it should produce more energy during its lifetime than is required to manufacture it. In this study we evaluate the primary energy requirements of a prospective renewable energy technology, solar-driven photoelectrochemical (PEC) production of hydrogen from water. Using a life cycle assessment (LCA) methodology, we evaluate the primary energy requirements for upstream raw material preparation and fabrication under a range of assumptions of processes and materials. As the technology is at a very early stage of research and development, the analysis has considerable uncertainties. We consider and analyze three cases that we believe span a relevant range of primary energy requirements: 1550 MJ m<sup>-2</sup> (lower case), 2110 MJ m<sup>-2</sup> (medium case), and 3440 MJ m<sup>-2</sup> (higher case). We then use the medium case primary energy requirement to estimate the net primary energy balance (energy produced minus energy requirement) of the PEC device, which depends on device performance, e.g. longevity and solar-to-hydrogen (STH) efficiency. We consider STH efficiency ranging from 3% to 10% and longevity ranging from 5 to 30 years to assist in setting targets for research, development and future commercialization. For example, if STH efficiency is 3%, the longevity must be at least 8 years to yield a positive net energy. A sensitivity analysis shows that the net energy varies significantly with different assumptions of STH efficiency, longevity and thermo-efficiency of fabrication. Material choices for photoelectrodes or catalysts do not have a large influence on primary energy requirements, though less abundant materials like platinum may be unsuitable for large scale-up.

Received 13th March 2013  
Accepted 5th June 2013

DOI: 10.1039/c3ee40880a

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## Broader context

Long term concerns about climate change and fossil fuel depletion will require a transition towards energy systems powered by solar radiation or other renewable sources. Existing solar energy systems have critical constraints that may limit their scale-up, such as land-use requirements for biomass-based systems, and lack of inexpensive large-scale storage options for photovoltaic electricity. A solar-driven photoelectrochemical (PEC) water-splitting device could generate storable chemical fuel (hydrogen) directly from water and sunlight. The global research attention on PEC technology and its application has been increasing in recent years. However, a fundamental requirement for a renewable energy generation technology is that it should produce more energy during its lifetime than is required to manufacture it. No such net energy analysis of PEC devices has been published to date. In this study we use a life cycle assessment (LCA) methodology to evaluate the primary energy requirements for production of PEC devices, and present net energy results under a range of assumptions of fabrication processes, materials, solar-to-hydrogen efficiency and device longevity.

## 1 Introduction

Solar energy is an abundant resource that could provide a potential solution to address the challenge of increasing global energy demand and depleting fossil fuel resources.<sup>1,2</sup> However, the intermittency of sunlight makes it challenging to integrate

solar energy into energy systems on a large scale. Photovoltaic (PV) systems capture and convert solar energy to electricity, but electricity storage in batteries is expensive and storage by other means (e.g. hydro-pumping, compressed air storage) is often limited by geographic conditions.<sup>3,4</sup> Converting solar energy directly to a chemical fuel could overcome these energy storage challenges. Photosynthesis in plants is a natural solar-to-fuel conversion process, but has a relatively low solar to stored energy efficiency (1 to 3%).<sup>5</sup> Much higher efficiencies may be possible using engineered devices designed to convert solar energy to fuel.<sup>6</sup> Focusing here on the solar generation of hydrogen (H<sub>2</sub>) from water, a number of pathways are potentially available including thermo-chemical, electro-chemical and

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photoelectrochemical processes.<sup>7</sup> In this study, we analyze a photoelectrochemical (PEC) process to generate hydrogen directly from water and solar energy at room temperature. This type of PEC process, also known as artificial photosynthesis,<sup>8</sup> artificial leaf,<sup>9</sup> or solar water splitting,<sup>10</sup> may be a possible solution for large-scale implementation of solar-produced fuel and therefore circumvent the limitations faced by PV and natural photosynthesis.<sup>11</sup>

For PEC generation of hydrogen to contribute to future energy generation at a relevant level world-wide, it must be cost competitive with other types of energy technology, both renewable and non-renewable, which are available at the time. However, the technology is still at an early stage of development and few either large-scale or long-duration demonstrations have been performed. A techno-economic analysis has been performed which estimated costs (\$ per kg H<sub>2</sub>) for several designs ranging from particle-based systems to those involving solar concentration.<sup>12</sup> While it is difficult to accurately estimate costs for an emerging technology, we feel that a more fundamental evaluation, namely a net primary energy analysis, can be valuable and insightful. Here we evaluate the primary energy requirement of manufacturing a range of PEC devices and thus estimate the net energy gain as a function of the efficiency and longevity of the device.

## 2 Methodology – net energy analysis

### 2.1 Primary energy requirement and net energy balance

Although available solar radiation is free to use, a device to collect and apply solar energy may come at an energy cost. To understand the relative merits of different technologies, the energy required and energy produced can be compared to determine the life-cycle energy implications of technologies used to harvest solar energy.

Various metrics can be used to quantify aspects of energy technologies. A fundamental metric is the *primary energy requirement*, which includes all energy used from extraction of natural resources, preparation of upstream materials, and each step of manufacturing the delivered device. For example, previous analyses have found a primary energy requirement of 2730 MJ m<sup>-2</sup> for multi-crystalline Si PV,<sup>13</sup> 1500 MJ m<sup>-2</sup> for thin-film CdTe PV,<sup>14</sup> and 860 MJ m<sup>-2</sup> for triple-junction amorphous Si PV.<sup>15</sup>

To compare the energy required and energy produced, a more suitable metric is the system *net energy balance*, defined as the available energy output per unit of the device or final product, minus the primary energy requirement to produce the device.<sup>16</sup> If the net energy balance is negative, the energy produced is less than energy required to produce the device.

Decision-making regarding energy technologies should be based on full life cycle environmental impacts, comparing various impact types and their damages.<sup>17</sup> A range of other environmental issues may be associated with PEC devices and should be considered, such as water use, land use and regional climate consequences.<sup>18</sup> In addition to energy and environmental considerations, economic considerations are also critical, as noted by a recent report which evaluated the cost of PEC devices,<sup>12</sup> though of different designs than the PEC device modeled in the present study.

### 2.2 System boundaries and functional units

The principles and framework that guide the present study are based generally on the ISO 14040 framework for Life Cycle Assessment (LCA).<sup>19</sup>

The system boundary and functional units of this LCA study are shown in Fig. 1. We analyze the primary energy requirement (inputs for materials and fabrication processes) in MJ per m<sup>2</sup> PEC. We then consider the performance of the PEC at capturing solar energy, by estimating the energy production in units of MJ of hydrogen produced per m<sup>2</sup> PEC. Finally, we present the primary energy requirement in units of MJ per kg of hydrogen produced, and determine the net energy implications of the technology.

The system boundaries of this study are limited to the materials and fabrication processes of device-level PEC components, including electrodes, catalysts, membrane, and encapsulation. Peripheral structures, *e.g.* water tanks, piping, manifolds, and hydrogen handling infrastructure, are beyond the scope of the present analysis. These broader system components may be significant, and should be investigated in future studies.

The inventory of primary energy requirements for each component of a PEC device is obtained by a variety of methods. Data on some common materials (*e.g.* metals, plastics) are included in life cycle inventory (LCI) databases, *e.g.* Ecoinvent Version2.<sup>20</sup> For some materials (*e.g.* the membrane) that are not found in LCI databases or literature reviews, we use representative data on proxy materials. For fabrication processes that have not been evaluated before, *e.g.* the vapor-liquid-solid growth process,<sup>21</sup> we use thermodynamic modeling to provide bounding estimates.<sup>22</sup> In general, we find that future efforts to integrate and collate first-hand data on PEC technology and related micro-scale fabrication processes would be of great use to LCA practitioners and system designers.

### 2.3 Challenges and opportunities

LCA is more challenging when the analyzed technology is still at an early-stage of research and development (R&D), with many

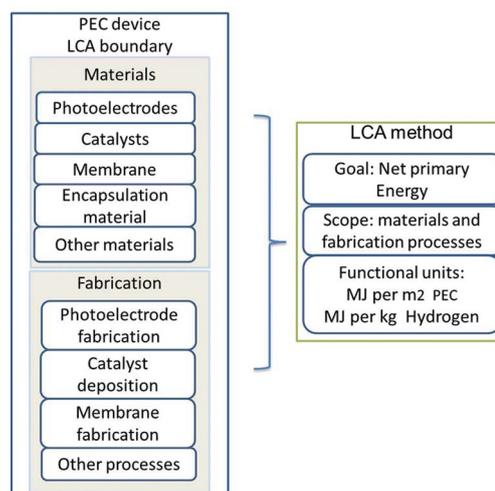


Fig. 1 LCA study of PEC device – goal, scope, functional unit and boundary.

uncertainties regarding potential scale-up pathways. The present study faces several particular challenges: paucity of LCI data on PEC materials and processes; the use of emerging and sparsely documented nano/micro-structured materials (*e.g.* silicon wire arrays) in the technology; and scale-up uncertainties of fabrication processes between laboratory-scale and industrial-scale techniques.

Although the LCA of early-stage R&D technology faces many challenges, its potential benefits to stakeholders are tremendous. It could help fundamental scientists to envision a larger context for their research efforts. Ideally, early-stage LCA may assist in selection of materials, allow system-wide design optimization, and reduce negative environmental impacts even at very early stages of R&D.

### 3 Principle of PEC device and assumptions of material choice and fabrication

#### 3.1 Principle of PEC device

The solar-to-hydrogen PEC process is designed to use semiconductor materials, water-splitting catalysts and electrodes to convert sunlight and water into hydrogen, mimicking some steps of the natural process of photosynthesis.<sup>10,23</sup> Here, we consider a tandem arrangement with an oxygen-generating photoanode and a hydrogen-generating photocathode in series, as these types of designs have the highest reported laboratory efficiencies to date.<sup>24,25</sup> In simple terms, the tandem-PEC is based on the following functions: (1) excitation of electron-holes by solar energy and their separation; (2) oxidation of water at the photoanode by holes; (3) transport of protons from

photoanode to photocathode through a membrane (which also acts to separate hydrogen and oxygen); (4) reduction of hydrogen ions at the photocathodes by electrons.<sup>6,26</sup> Both reactions could use catalysts to make the reactions more efficient.<sup>26–28</sup> A PEC device also requires a transparent cover, a support structure, and encapsulation.

The conceptual structure of a PEC device is shown in Fig. 2. It shows the layered-structure of a PEC device with glass cover, photoanode, membrane, photocathode and chamber.

#### 3.2 Assumptions of material choice and fabrication

We analyze two major uncertainties that influence the primary energy requirement of a PEC device: (1) material choice (types and quantities), and (2) fabrication parameters. For each source of uncertainty related to material choice and fabrication, the assumptions of the lower, medium and higher cases are shown in Table 1.

Our medium case assumed the use of  $\text{WO}_3$  for the photoanode, though other materials (*e.g.* GaAs,  $\text{BiVO}_4$ ) could also be used to achieve higher STH efficiency. In terms of the primary energy requirement, we believe that  $\text{WO}_3$  represents the lower case for photoanode material, GaAs represents the higher case, and other materials would fall between them. The catalyst for the photocathode in our medium case analysis is Pt. However, other materials, preferably earth-abundant, could also be used as catalysts, *e.g.* Co. We believe that for catalysts for the photocathode, Co represents the lower case and Pt represents the higher case. Our medium case assumes no catalyst for the photoanode, which also represents the lower case. Materials such as Pt, Ru, or Ir could be used as catalysts for the photoanode. We select Pt as the higher case material due to the availability of life cycle inventory data on Pt and to the larger production quantities of Pt. For encapsulation materials, our medium case assumes the use of PVC, because it is a mature technology for which life-cycle data are available. However other materials may also be used, and we select polycarbonate for the higher case encapsulation material.

Quantifying the material and energy flows of advanced fabrication processes (*e.g.* photoelectrode and membrane fabrication) is challenging. We use a simple thermodynamic

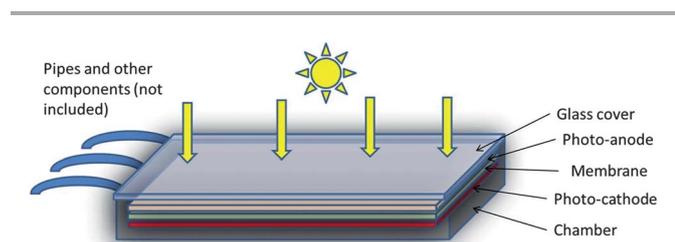


Fig. 2 Conceptual structure of a tandem solar-to-hydrogen PEC device.

Table 1 Assumptions of lower, medium and higher cases of uncertainty analysis

Category	Component	Lower case <sup>a</sup>	Medium case <sup>a</sup>	Higher case <sup>a</sup>
Material choices	Photocathode	Silicon (Si)	Silicon (Si)	Silicon (Si)
	Photoanode	Tungsten trioxide ( $\text{WO}_3$ )	Tungsten trioxide ( $\text{WO}_3$ )	Gallium arsenide (GaAs)
	Catalysts for photocathode	Cobalt (Co)	Platinum (Pt)	Platinum (Pt)
	Catalysts for photoanode	No catalyst	No catalyst	Platinum (Pt)
	Encapsulation	Polyvinyl chloride (PVC)	Polyvinyl chloride (PVC)	Polycarbonate
	Thickness of chamber	3 mm	5 mm	7 mm
	Thickness of membrane	30 $\mu\text{m}$	50 $\mu\text{m}$	70 $\mu\text{m}$
Fabrication	Thermodynamic efficiency of processes used to fabricate photocathode/anode and membrane	70%	50%	30%

<sup>a</sup> The lower, medium and higher cases are terms describing the primary energy requirement in  $\text{MJ kg}^{-1}$  of hydrogen, not the parameter values, *e.g.* a higher efficiency of the fabrication process leads to lower values for the primary energy requirement.

model to estimate the theoretical energy use of fabrication processes, assuming ideal conditions and control. In other words, this model gives results for 100% thermo-efficiency. In our medium case analysis, these theoretical results were adjusted assuming 50% thermo-efficiency. We also present analyses of a lower case of the primary energy requirement assuming 70% thermo-efficiency, and a higher case assuming 30% thermo-efficiency. More details of the three cases are found in Section 4.

## 4 Primary energy requirements

There are four main steps to fabricate a PEC device: (1) photo-electrode fabrication and catalyst deposition; (2) membrane fabrication; (3) device encapsulation; and (4) other ancillary processes. For each step, the primary energy requirement is calculated as the sum of two parts: (i) energy requirement for upstream materials production and (ii) energy requirement for fabrication processes.

### 4.1 Photoelectrode fabrication and catalyst deposition

Silicon (Si) is an attractive candidate for a tandem-system photocathode, and the structure of Si micro-wire arrays could enhance the energy-conversion efficiencies compared to values achieved by conventional planar-structured Si photocathodes.<sup>29</sup> Studies by Boettcher *et al.*<sup>21,29</sup> provide detailed growth procedures and conditions (*e.g.* temperature, pressure). The Si wires are grown by a template vapor-liquid-solid growth process in a chemical vapor deposition (CVD) system. The wires are approximately 2.8  $\mu\text{m}$  in diameter and 40–60  $\mu\text{m}$  in length. A catalyst, here assumed to be platinum (Pt), is deposited by electron beam evaporation on these Si micro-wires. However, other materials could also be used as catalysts, *e.g.* cobalt (Co) described by Reece *et al.*<sup>10</sup>

For photoanode materials, tungsten trioxide ( $\text{WO}_3$ ), titanium dioxide ( $\text{TiO}_2$ ), gallium arsenide (GaAs), bismuth vanadium oxide ( $\text{BiVO}_4$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ) and others have been reported.<sup>26</sup> None of them is an ideal candidate considering both efficiency and longevity and there is need for more research on photoanode materials. Catalysts could also be deposited on photoanodes. In our medium case, we consider  $\text{WO}_3$  as a material for the photoanode (without a catalyst), and Si for the photocathode (with Pt as a catalyst). This combination is a hypothetical design that may not have sufficient voltage for water-splitting. We use this as our medium case because data are available on  $\text{WO}_3$  micro-wire array growth using a vapor-solid CVD process,<sup>30</sup> and we observe that the embodied energy of all potential photoanode upstream materials is very small compared to other components of the device (see Section 4.5). Table 2 lists the estimated primary energy requirements for upstream materials of a Si wire array,  $\text{WO}_3$  wire array and Pt.

We conducted a preliminary scale-up analysis to estimate required quantities of catalyst materials and to identify potential constraints in material availability. We adopt the “H2 Case” scenario from the European Commission’s World Energy

**Table 2** Estimated primary energy requirements for the upstream materials of the photoelectrodes and catalyst

Materials	Mass ( $\text{g m}^{-2}$ )	Energy intensity <sup>20</sup> ( $\text{MJ g}^{-1}$ )	Primary energy requirement ( $\text{MJ m}^{-2}$ )
Silicon (Si)	4.7 <sup>a,29</sup>	1.1	5.2
Tungsten trioxide ( $\text{WO}_3$ )	0.1 <sup>b,30</sup>	0.2	0.02
Platinum (Pt)	0.03 <sup>c,29</sup>	279	9.0

<sup>a</sup> Si micro-wires are 2.8  $\mu\text{m}$  diameter, 50  $\mu\text{m}$  length, and 7  $\mu\text{m}$  lattice spacing. <sup>b</sup>  $\text{WO}_3$  micro-wires are 70 nm diameter, 4  $\mu\text{m}$  length, and 0.5  $\mu\text{m}$  lattice spacing. <sup>c</sup> Pt deposition thickness is 1.5 nm.

Technology Outlook, with projected  $\text{H}_2$  production of 310 Tg ( $10^{12}$  gram) by the year 2050.<sup>31</sup> To produce this amount of hydrogen at STH efficiency of 10%, about 42 000  $\text{km}^2$  PEC panel area is required. At the Pt deposition rate listed in Table 2, this entails about 1400 t of Pt in use in PEC panels, which in principle could be recovered from degraded panels and recycled into new panels. This amount of Pt corresponds to about seven years’ of current mine production, which averaged 200 ton per year during the past decade.<sup>32</sup> While not presenting an absolute impediment to scale-up, the observed quantities of Pt relative to the modeled requirements suggest that Pt may not be the ideal catalyst material for large-scale deployment, and other materials such as Co<sup>10</sup> may be more suitable.

The fabrication process of the photoelectrodes and catalysts involves multiple steps of heating, vacuum pumping and plasma generation. These steps consume the majority of the energy during the wire array growth and catalyst deposition procedure. The determination of the power usage and primary energy requirement for future large-scale fabrication is challenging. We have found no previous publications documenting primary energy use of such vapor-liquid-solid processes. The primary energy use of CVD has been documented for the photovoltaic<sup>15</sup> and semiconductor<sup>33</sup> industries; however, those CVD processes are for deposition of planar-structured thin films, not micro-structured wire growth. Therefore, we do not believe such previous estimates should be applied for this technology. Direct measurement of the power usage for laboratory-scale experiments (typically at a production scale of 1  $\text{cm}^2$ ) would not represent meaningful energy use values for future mass-production fabrication equipment. To provide bounding estimates, in this study we use simple thermodynamic models to evaluate theoretical energy usage for heating and vacuum pumping processes assuming ideal insulation and control. Thermodynamic models require inputs in terms of the mass of the medium (gas or liquid). The thermodynamic models use the first law of thermodynamics and the ideal gas law at isothermal conditions, as defined in eqn (1) and (2).

$$E_h = C_p \times M \times (T - T_0) \quad (1)$$

where  $E_h$  is the energy required for heating in kJ,  $C_p$  is the specific heat of the medium in  $\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ ,  $M$  is the mass of the

medium in kg,  $T$  is the required temperature in °C, and  $T_0$  is the initial temperature in °C.

$$E_p = V \times P_0 \times \ln \frac{P_0}{P} \quad (2)$$

where  $E_p$  is the energy required for vacuum pumping in J,  $V$  is the volume in m<sup>3</sup>,  $P_0$  is the initial pressure in Pa, and  $P$  is the required pressure in Pa.

Such a fabrication system would have 100% thermo-efficiency, though in practice the efficiency would be lower. The theoretical values  $E_h$  and  $E_p$  in eqn (1) and (2) therefore represent lower bounds of the actual primary energy requirements.

The actual energy use will be the theoretical value divided by the thermo-efficiency ( $\eta$ ) of the process, represented by eqn (3). The thermo-efficiency will depend on several factors including insulation, control systems, and process optimization. While the energy efficiency of individual components such as boilers can be quite high (e.g. 80–95%), the overall efficiency of an entire system is typically much lower.<sup>34</sup> For example, steam heating systems deliver an average of only 55% of input energy to end-use processes, with the remaining energy lost due to inefficiencies in energy conversion and distribution. In the absence of more compelling data, in this study we have assumed a thermo-efficiency of 50% for our medium case.

$$E_{\text{actual}} = \frac{E_{\text{theoretical}}}{\eta} \quad (3)$$

where  $E_{\text{theoretical}}$  is  $E_h$  or  $E_p$ , and  $\eta$  is the thermo-efficiency of the process.

We assume that the energy use  $E_h$  or  $E_p$  represents energy in the form of electricity. To obtain the primary energy requirement, we apply an electricity-to-primary energy conversion factor of 0.29, which represents the efficiency of the average US grid mix.<sup>15</sup> Table 3 lists the estimated primary energy requirements for Si wire array growth (photocathode), WO<sub>3</sub> wire array growth (photoanode) and Pt (catalyst) deposition on Si wires. It also lists the required temperature and pressure for each reaction step.

## 4.2 Membrane fabrication

Membranes of PEC devices need to be transparent, impermeable to the produced hydrogen and oxygen, and conductive to protons (or hydroxide).<sup>35</sup> The most commonly used membrane material is perfluoro-sulfonic acid (PFSA), available commercially as Nafion®.<sup>36</sup> Staffell and Ingram<sup>37</sup> estimated the primary energy requirement for producing PFSA membranes to be 16 times higher than for producing polyethylene. The primary energy used to produce polyethylene is 78 MJ kg<sup>-1</sup>,<sup>20</sup> thus the amount of energy used to produce PFSA is estimated at 1248 MJ kg<sup>-1</sup>. To assess the accuracy of this estimate, we employ one of the concepts used in economic input–output life cycle assessment (EIO-LCA) which assumes that products in the same sector of an input–output table have the same energy intensity (MJ per \$), therefore the primary energy requirements of two products in the same sector are proportional to their costs.<sup>38</sup> The cost of PFSA is estimated at 35 \$ per m<sup>2</sup> for mass production<sup>39</sup> and the cost of polyethylene (a proxy material from the

same industrial sector) is 2 \$ per m<sup>2</sup> (Sigma Aldrich). Correspondingly, the primary energy of producing PFSA is estimated to be 18 times that of polyethylene, or 1404 MJ kg<sup>-1</sup>. The required thickness of PFSA membrane depends on the device design and is assumed to total 50 μm<sup>40</sup> for our medium case. Overall, assuming a 1.58 g cm<sup>-3</sup> density of PFSA,<sup>41</sup> the primary energy requirement for preparing the membrane material PFSA is estimated to be 139 MJ m<sup>-2</sup>.

Additionally, the procedure of embedding a photoelectrode wire array into the membrane (membrane fabrication) also consumes primary energy. The procedure of membrane fabrication was discussed in detail by Spurgeon *et al.*<sup>40</sup> Here we use the thermodynamic model given by eqn (1) to estimate a lower bound for the primary energy requirement for the electrode-membrane fabrication. As for the fabrication of photoelectrodes, we assume 50% thermo-efficiency for the medium case. The primary energy requirement is estimated to be 166 MJ m<sup>-2</sup> for the medium case.

To connect two layers of membrane with embedded photocathode and photoanode wire arrays, an intervening layer of poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) is used.<sup>40</sup> The primary energy requirement of PEDOT-PSS with a thickness of 20 μm was reported as 4.7 MJ m<sup>-2</sup> in a LCA study of polymer solar cells.<sup>42</sup>

## 4.3 PEC device encapsulation

The supporting materials considered in this study are used for encapsulation of the photoelectrodes and membrane in a sealed chamber. The cover material needs to be transparent to sunlight. We chose flat glass which has a production energy intensity of 15 MJ kg<sup>-1</sup>.<sup>20</sup> Additional encapsulation material is needed for holding the whole structure and containing the liquid and gases. We chose a widely-used plastic, polyvinyl chloride (PVC), with a production energy intensity of 70 MJ kg<sup>-1</sup>.<sup>20</sup> The area of the cover and encapsulation material is the same as the other layers, which are assumed to be 1 m<sup>2</sup>. For the medium case analysis, the thickness of glass is assumed to be 3 mm and thickness of PVC is assumed to be 5 mm. Additional encapsulation steps (e.g. cutting, pressing) and energy requirements are assumed to be negligible, compared to the energy-intensive material production procedures. The estimated total primary energy requirement for the glass cover is 114 MJ m<sup>-2</sup> and for the PVC encapsulation material is 420 MJ m<sup>-2</sup>.

## 4.4 Other ancillary processes

Besides the direct primary energy requirements for PEC device fabrication and encapsulation, there are primary energy requirements for other ancillary materials (e.g. miscellaneous chemicals) and indirect industrial processes (e.g. environmental control of manufacturing facilities). Similar to the photovoltaic<sup>13–15</sup> and semiconductor<sup>43</sup> industries, some inevitable ancillary primary energy requirements should be included in a comprehensive LCA analysis of PEC devices. We include a value of 15 MJ m<sup>-2</sup> for other miscellaneous chemicals, adjusted from a silicon-PV LCA study<sup>13</sup> that reported primary energy requirement for residual miscellaneous materials using

**Table 3** Estimated medium-case primary energy requirements for photoelectrodes wire growth and catalyst deposition

Procedures of fabrication	Theoretical values (100% thermo-efficiency)	Conditions <sup>29,30</sup>	Medium case (50% thermo-efficiency)
<b>Heating for Si wire growth</b>	$E$ (MJ m <sup>-2</sup> )	<b>Temperature <math>T</math> (°C)</b>	$E$ (MJ m <sup>-2</sup> )
Annealing under H <sub>2</sub>	135.2	1000	
Curing under dichloromethane	71.0	75	
Etching under HCl	64.7	75	
Annealing under N <sub>2</sub>	48.7	650	
Thermal oxidation under O <sub>2</sub>	0.3	1100	
Heating under N <sub>2</sub>	0.2	850	
<b>Plasma generation for Si wire growth</b>	$E$ (MJ m <sup>-2</sup> )	<b>Power (kW)</b>	
Wax etching	5.0	0.4	
<b>Vacuum pumping for Si wire growth</b>	$E$ (MJ m <sup>-2</sup> )	<b>Pressure (Pa)</b>	
Wax etching	2.7	4.0	
<b>Total of Si wire growth</b>	328		656
<b>Heating for WO<sub>3</sub> wire growth</b>	$E$ (MJ m <sup>-2</sup> )	<b><math>T</math> (°C)</b>	$E$ (MJ m <sup>-2</sup> )
Growing under air	165.5	1000	
<b>Vacuum pumping for WO<sub>3</sub> wire growth</b>	$E$ (MJ m <sup>-2</sup> )	<b>Pressure (Pa)</b>	
Vapor transport	1.0	$2.0 \times 10^3$	
<b>Total of WO<sub>3</sub> wire growth</b>	166		332
<b>Vacuum pumping for Pt deposition</b>	$E$ (MJ m <sup>-2</sup> )	<b>Pressure (Pa)</b>	$E$ (MJ m <sup>-2</sup> )
Electronbeam deposition of Pt	6.4	$8.0 \times 10^{-4}$	
<b>Total of Pt deposition</b>	6.4		13

**Table 4** Estimated primary energy requirements (materials and fabrication/encapsulation) for each component in PEC device (medium case)

Processes	Components	Medium-case energy requirement (MJ m <sup>-2</sup> )	Percentage of total
Photoelectrodes fabrication and catalysts deposition	Photocathode wire array growth	656	31.0%
	Photocathode material	5	0.2%
	Photoanode wire array growth	332	15.7%
	Photoanode material	Negligible	0.0%
	Catalyst deposition	13	0.6%
	Catalyst material	9	0.4%
Membrane and intervening layer fabrication	Membrane fabrication	166	7.8%
	Membrane material	139	6.6%
	Intervening layer fabrication	Negligible	0.0%
Device encapsulation	Intervening layer material	5	0.2%
	Encapsulation processes	Negligible	0.0%
	Chamber material	420	19.9%
	Cover material	114	5.4%
Ancillary processes	Environmental control	200	9.5%
	Water pumping	31	1.5%
	Miscellaneous chemicals	15	0.7%
	Cleaning	10	0.5%
<b>Total</b>		<b>2114</b>	<b>100%</b>

EIO-LCA; 31 MJ m<sup>-2</sup> for water pumping and 10 MJ m<sup>-2</sup> for cleaning, adjusted from a thin-film PV LCA study<sup>15</sup> that reported primary energy requirement for water pumping and cleaning during deposition processes; and 200 MJ m<sup>-2</sup> for environmental control, adjusted from a thin-film PV LCA study<sup>14</sup> that reported ancillary process energy for space heating, cooling and ventilation.

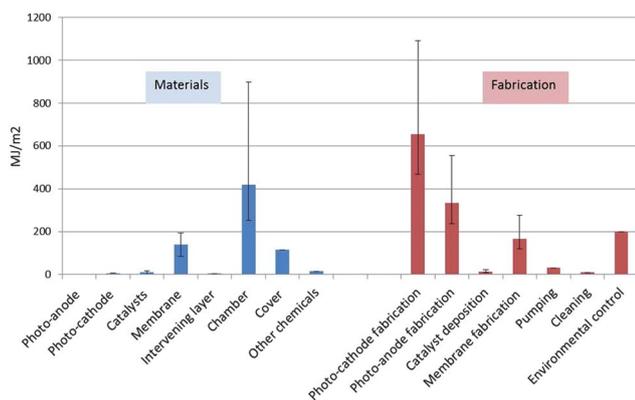
#### 4.5 Results of primary energy requirement

Results in Table 4 show the estimated medium case primary energy requirements for each process discussed in the previous sections, including both material preparation and fabrication/encapsulation processes. The total primary energy requirement for a PEC device is estimated to be 2110 MJ m<sup>-2</sup> in the medium case.

Table 5 shows the primary energy requirement of PEC for the lower, medium and higher cases. Fig. 3 shows the primary energy requirement for each component of material use and fabrication

**Table 5** Estimated primary energy requirement of PEC device in MJ m<sup>-2</sup> for lower, medium and higher cases

Primary energy requirement of PEC (MJ m <sup>-2</sup> )	Lower case	Medium case	Higher case
Materials	470	710	1250
Fabrication	1070	1410	2190
<b>Total</b>	<b>1550</b>	<b>2110</b>	<b>3440</b>



**Fig. 3** Estimated medium case primary energy requirement for each component in a PEC device in  $\text{MJ m}^{-2}$ , with error bars showing lower and higher case bounds.

processes with a range of results for the lower and higher cases. The various assumptions of the thermo-efficiency of the fabrication processes and the material choice for encapsulation introduce significant uncertainties, while the material choices of the photoanode/photocathode or catalyst do not.

## 5 Performance parameters and net energy balance

To calculate the primary energy for making the PEC device in units of MJ per kg of produced hydrogen, the primary energy requirement in  $\text{MJ m}^{-2}$  is divided by the amount of hydrogen produced during the lifetime of the PEC device. The amount of hydrogen produced is determined by the performance parameters of the PEC device, *i.e.* the solar-to-hydrogen (STH) efficiency and the device longevity. Currently, since the technology is at an early stage of R&D, there are significant uncertainties regarding future achievements of STH efficiency and longevity.

### 5.1 Performance parameters – STH and longevity

To standardize the definition of efficiency, Chen *et al.* proposed solar-to-hydrogen (STH) efficiency as a benchmark efficiency suitable for mainstream reporting.<sup>44</sup> STH efficiency describes the overall energy efficiency of a PEC water-splitting device exposed to broadband solar Air Mass 1.5 Global (AM1.5G) illumination under zero bias conditions. STH efficiency is defined in eqn (4).

$$\text{STH} = \frac{(\text{H}_2 \text{ production}) \times (\text{Gibbs of H}_2)}{(\text{solar intensity}) \times (\text{area})} \quad (4)$$

where  $\text{H}_2$  production is the hydrogen production rate in  $\text{mmol s}^{-1}$ , Gibbs of  $\text{H}_2$  is the Gibbs free energy of  $\text{H}_2$  in  $\text{J mol}^{-1}$ , solar intensity is in  $\text{mW cm}^{-2}$ , and area is the exposed area of the PEC device in  $\text{cm}^2$ .

The variable of particular interest to this study is the hydrogen production rate under a given STH efficiency. Based on eqn (4), after unit conversion, and ignoring the small difference between Gibbs free energy and Lower Heating Value (LHV) of hydrogen at ambient temperature,<sup>44</sup> the hydrogen production rate is defined in eqn (5).

$$\text{H}_2 \text{ production} = \frac{(\text{solar intensity}) \times (\text{STH})}{\text{LHV of H}_2} \quad (5)$$

where hydrogen production is in kg per day per  $\text{m}^2$ , solar intensity is in  $\text{kW h per day per m}^2$ , and LHV of  $\text{H}_2$  is in  $\text{kW h kg}^{-1}$ .

The LHV of hydrogen is constant at  $33 \text{ kW h kg}^{-1}$ . From eqn (5), therefore, STH and solar intensity are the two key parameters that determine the hydrogen production rate. Solar intensity under the AM1.5G condition is  $6.57 \text{ kW h per day per m}^2$  in a sun-abundant area (*e.g.* Phoenix, Arizona, USA).<sup>45</sup> In that region, for example, if STH efficiency is 10%, hydrogen produced by  $1 \text{ m}^2$  of PEC device in a day is about 0.02 kg.

The reported longevity numbers for current PEC devices are on the scale of hours or days. For example, a cobalt-borate catalyzed silicon PEC cell worked stably in alkaline media for 24 hours,<sup>10</sup> and Ni–Mo electrodes reportedly worked in alkaline media for thousands of hours.<sup>46</sup> However, there are ways to potentially extend the life of a PEC device,<sup>47</sup> *e.g.* use less corrosive near-neutral electrolytes, adopt self-healing strategies,<sup>10</sup> and utilize semiconductor surface modifications.<sup>48</sup>

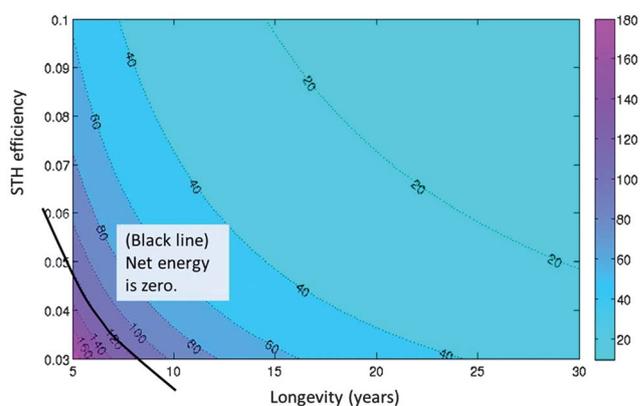
The lifetime primary energy requirement to produce 1 kg of hydrogen is defined in eqn (6).

$$\begin{aligned} &\text{Lifetime primary energy requirement of H}_2 \\ &= \frac{\text{primary energy requirement of PEC}}{(\text{H}_2 \text{ production}) \times (\text{longevity})} \end{aligned} \quad (6)$$

where lifetime primary energy requirement of  $\text{H}_2$  is in  $\text{MJ kg}^{-1}$ , primary energy requirement of PEC is in  $\text{MJ m}^{-2}$ ,  $\text{H}_2$  production is in  $\text{kg per day per m}^2$ , and longevity is in days.

### 5.2 Uncertainties and net energy balance

The analysis of uncertainties is important in LCA studies,<sup>49</sup> especially for technologies that are still at an early stage of laboratory-scale research. Both STH efficiency and longevity have significant uncertainties. In this analysis we use the medium case result, which has a primary energy requirement of  $2110 \text{ MJ m}^{-2}$ . The resulting primary energy required to produce 1 kg of hydrogen is shown in Fig. 4, with STH efficiency ranging



**Fig. 4** Primary energy (MJ) to produce 1 kg of hydrogen with various assumptions of solar-to-hydrogen efficiency and longevity (lower left part of the figure below the black line has negative net energy).

**Table 6** Net energy of hydrogen with various assumptions of efficiency and longevity (assuming the medium case of 2110 MJ m<sup>-2</sup> primary energy requirement for PEC production)

Efficiency	Longevity (years)	Primary energy requirement (MJ kg <sup>-1</sup> )	Energy content of hydrogen (MJ kg <sup>-1</sup> )	Net energy of hydrogen (MJ kg <sup>-1</sup> )
3%	5	194	120	(-) 74
3%	8	120	120	0
3%	10	97	120	13
3%	30	32	120	88
5%	5	116	120	4
5%	10	58	120	62
5%	30	19	120	101
10%	5	58	120	62
10%	10	29	120	91
10%	30	10	120	110

from 3% to 10% and longevity ranging from 5 years to 30 years. The primary energy required to produce 1 kg of hydrogen increases with lower STH efficiency and longevity. Because the energy content (LVH) of 1 kg of hydrogen is approximately 120 MJ,<sup>50</sup> when the primary energy of PEC increases to 120 MJ kg<sup>-1</sup> (the black line in Fig. 4), the net energy is zero. This means that the amount of energy required to make the device is equal to the energy it produces during its service life.

Table 6 shows the results for net energy of hydrogen with various levels of STH efficiency and longevity. With STH efficiency of 10% and longevity of 10 years, the primary energy requirement to produce 1 kg of hydrogen is estimated by eqn (6) to be 29 MJ. Because the energy content (LHV) of 1 kg of hydrogen is approximately 120 MJ,<sup>50</sup> the net energy yield of 1 kg of hydrogen produced by the PEC device is 91 MJ. With efficiency of 3% and longevity of 5 years, the net energy of hydrogen produced by the PEC device is negative. At higher levels of efficiency and/or longevity, the net energy is positive.

## 6 Sensitivity analysis

The uncertainty analysis indicates that some parameters (*e.g.* thermo-efficiency of photoelectrode fabrication, STH efficiency, and device longevity) could significantly influence the resulting primary energy requirement to produce 1 kg of hydrogen. To quantify the influence of each factor, we conduct a sensitivity analysis.

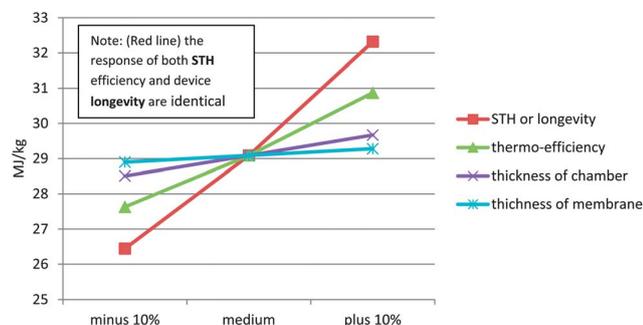
**Fig. 5** Perturbative sensitivity analysis of the primary energy requirement of producing 1 kg of hydrogen, with plus and minus 10% changes from the medium case (29 MJ kg<sup>-1</sup>).

Fig. 5 shows a perturbative sensitivity analysis of the primary energy requirement to produce 1 kg of hydrogen. The center point of the figure is the primary energy requirement of 29 MJ kg<sup>-1</sup>, based on the medium case assumptions for fabrication and materials, a STH efficiency of 10%, and device longevity of 10 years. The effect of varying each parameter by plus and minus 10% is shown. Changes in STH efficiency and longevity have the same effect, and cause the highest perturbation of the results.

Since the PEC technology is still at an early stage of R&D, some parameters are highly uncertain, *e.g.* the longevity and STH efficiency that PEC devices may achieve in the future. These results indicate which parameters are particularly critical for success of the technology, to guide basic researchers in prioritizing research objectives. As the technology becomes more mature, the uncertainties will be reduced as estimates of feasible levels of PEC device efficiency and longevity become more refined.

## 7 Comparing micro-structured and planar-structured PEC devices

The PEC structure with a micro-wire photoanode and photocathode that we analyzed in the previous sections is not the only design option. A planar-structured PEC could also be a promising design. For example, Reece *et al.* reported the design of a planar-structured PEC involving depositing a catalyst (cobalt) on a commercial triple-junction amorphous silicon PV cell.<sup>10</sup> The reason for introducing micro-structured wires is to enhance the STH efficiency;<sup>29</sup> however, this may come at the cost of a higher primary energy requirement compared with planar-structured PEC devices. Estimating the primary energy requirement of a planar-structured PEC is more straightforward compared with a micro-structured PEC. The main component of a planar-structured PEC is the triple-junction amorphous silicon PV cell. Kim and Fthenakis<sup>15</sup> estimated the primary energy requirement for triple-junction amorphous silicon PV cells at 860 MJ m<sup>-2</sup>. Our analysis shows that the primary energy used for catalyst material and deposition is small (9 and 13 MJ m<sup>-2</sup> respectively). For cobalt in particular, the primary energy embodied in the material is negligible. Assuming other

components, e.g. membrane, device encapsulation and ancillary processes are the same, and have the same primary energy requirement as in the medium case (micro-structured PEC), the total primary energy requirement for a planar-structured PEC would be  $1980 \text{ MJ m}^{-2}$ . The efficiency of a planar-structured PEC (wireless) was reported as 2.6%.<sup>10</sup> If we assume the longevity to be 20 years, according to eqn (6) the primary energy to produce 1 kg hydrogen would be  $52 \text{ MJ kg}^{-1}$ . To achieve the same net energy value, the STH efficiency of micro-structured PEC device (with a primary energy requirement of  $2110 \text{ MJ m}^{-2}$ ) would need to be marginally higher at 2.8%.

## 8 Conclusions

In this study we estimated the primary energy requirement for making a solar water-splitting PEC device with a micro-structured photocathode and photoanode, and conducted a net energy analysis for hydrogen production. There are four main processes during device fabrication: photoelectrode fabrication and catalyst deposition; membrane and intervening layer fabrication; device encapsulation; and ancillary processes. In each step, primary energy requirements for the PEC device were calculated as the sum of energy requirements for the upstream materials production and fabrication processes. We found that the total primary energy requirement for producing the PEC device is about  $2110 \text{ MJ m}^{-2}$  in our medium case, and could range from a low of 1550 to a high of  $3440 \text{ MJ m}^{-2}$ . The most energy-intensive process is the fabrication of the photoelectrodes, which represents 50% of the primary energy requirement. Other key components of the PEC device include the membrane (Nafion®) that uses 15% of the production energy, and the catalyst (Pt) that uses 1% of the energy. Compared with multi-crystalline Si PV that has a primary energy requirement of  $2730 \text{ MJ m}^{-2}$ ,<sup>13</sup> the PEC device requires less energy to manufacture in our low and medium case analyses, but more energy in our higher case analysis.

We conducted a net energy analysis using a functional unit of primary energy (MJ) needed to produce 1 kg of hydrogen. The solar-to-hydrogen (STH) efficiency and longevity of the PEC device are key parameters in this net energy analysis, but because the technology is still at an early stage of development, the efficiency and longevity have significant ranges of uncertainty. We evaluated a wide range of plausible STH efficiencies and device longevity. For our medium case analysis with a 10 year longevity and 10% STH efficiency, the primary energy requirement is 29 MJ per kg of hydrogen, giving a net energy balance of  $91 \text{ MJ kg}^{-1}$ . Our uncertainty analysis shows that the primary energy required to produce 1 kg of hydrogen varies significantly with different assumptions of STH efficiency, device longevity and thermo-efficiency of fabrication. Material choices for photoelectrodes or catalysts do not have a major influence on the primary energy requirement, though less abundant materials like platinum may be unsuitable for large scale-up. Finally, we compared the results with a planar-structured PEC that has an estimated primary energy requirement of  $1980 \text{ MJ m}^{-2}$  and  $52 \text{ MJ per kg}$  hydrogen produced (assuming 2.6% efficiency and 20 year longevity). To achieve similar values

of primary energy requirement, the efficiency of a medium-case micro-structured PEC device would need to be 2.8%.

## Acknowledgements

This research was supported by Laboratory Directed Research and Development funding at the Lawrence Berkeley National Laboratory (LBNL), which is operated for US Department of Energy under Contract Grant no. DE-AC02-05CH11231 (Zhai, Ager, Sathre, Greenblatt and McKone). The work was also supported in part by the Joint Center for Artificial Photosynthesis (JCAP), a DOE Energy Innovation Hub, supported through the Office of Science of the US Department of Energy under Award no. DE-SC0004993 (Haussener and Walczak).

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