Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Design and cost considerations for practical solar-hydrogen generators

(Electronic Supplementary Information)

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1. Model Development

The photovoltaic's (PV) output curve from the 11% efficient triple junction a-Si/a-Si/µc-Si cell at AM 1.5 illumination and various concentration factors (CX) was provided to us by The Swiss Center for Electronics and Microtechnology, CSEM. A set of representative curves are shown below.

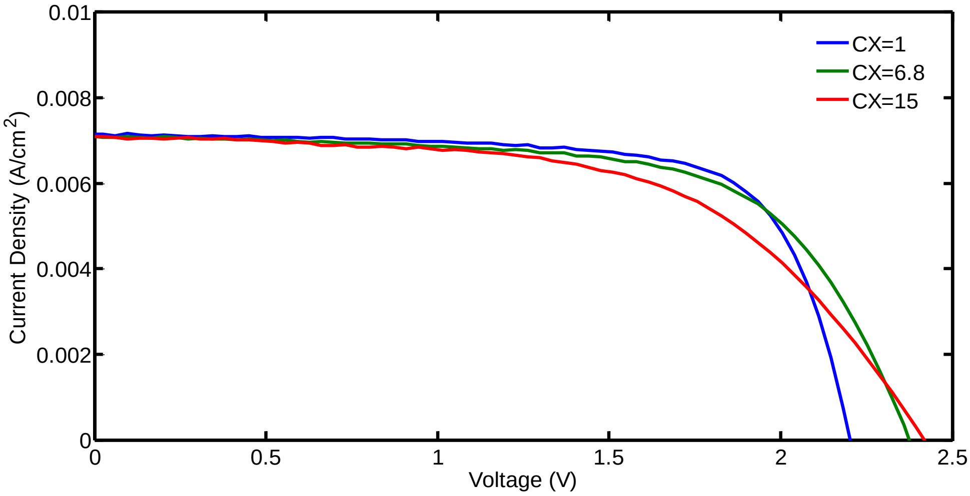

Figure S1: Output curve for a 11% a-Si/a-Si/µc-Si used in this study.

The PV' s output curve was adjusted according to the annual irradiation of a high radiation zone in Arizona. Average hour irradiance values per month were used to calculate the amount of kilograms produced hourly by the system. [1, 2] For the solar concentration study, we have considered a 15% of the irradiation is lost due to light scattering.

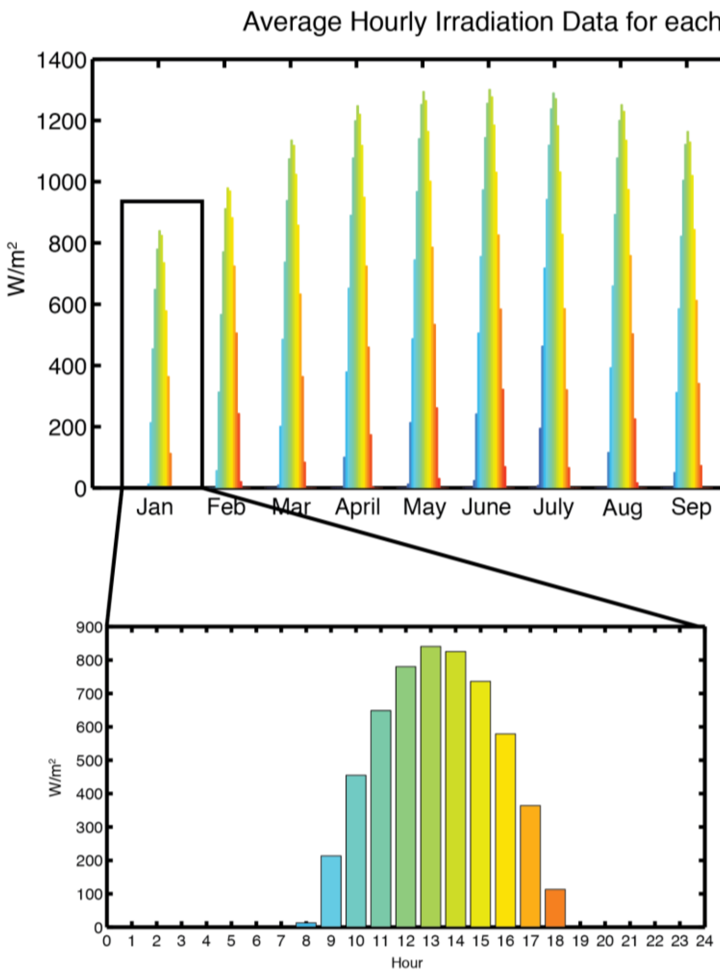

Figure S2: Average Hourly Irradiation Data used in this study

Electrolyzer's load curve

The IV curve of the electrolyzer was modeled using the equation below.

$$V = 1.23V + \eta_{anode} + \eta_{cathode} + \eta_{ohm}$$

The overpotential of the anode (η_{anode}) and the cathode ($\eta_{cathode}$) at the surface of the catalyst were modeled using the Butler-Volmer Equation.

$$J = J_0 * \left\{ e^{\frac{\alpha_a n F \eta}{RT}} - e^{\frac{-\alpha_c n F \eta}{RT}} \right\}$$

where:

- J_0 : is the exchange current density [A/cm^2]
- α_a, α_c: is the charge transfer coefficient of the anode and the cathode, respectively
- T: is temperature [K]
- n: was given a value of 2 for the empirical fitting of J_0 and α
- F: is the Faraday constant
- R: is the universal gas constant

The overpotential of the membrane (V_{ohm}) was modeled using:

$$V_{ohm} = \frac{jd}{\sigma};$$

where:

- j: is current density [A/cm^2]
- d: is the membrane's thickness. In this case we used 177 μm
- σ: is the membrane's conductivity in $S/_{cm}$. For Nafion we used 0.1 $S/_{cm}$

The model used for the overall current density at the catalyst layer was the following:

$$J = jA_{cat}fF$$

where:

- j: is current density in A/cm^2 at the surface of the catalyst particles
- A_{cat}: is the total surface area of catalytic particles
- f: is the fraction of catalyst surface that is active in the catalyst layer
- F: result of optimization of geometric factor, dimensionless

Here it is important to acknowledge that the value for the catalyst load in the catalyst layer (0.5 mg/cm^2) is similar to industrial platinum-based catalytic layers. The impact of this value over the cost of kilogram of hydrogen was studied carefully in the sensitivity analysis.

2. Catalytic parameters for anode and cathode materials

The catalytic parameters (J_0, α) used to model the electrolyzer's load curve were obtained from empirical fittings of catalysts Tafel plots for various catalysts, as reported elsewhere [3]. For each of the chosen materials, several data points were fitted to the Butler-Volmer equation in order to obtain parameters J_0, α.

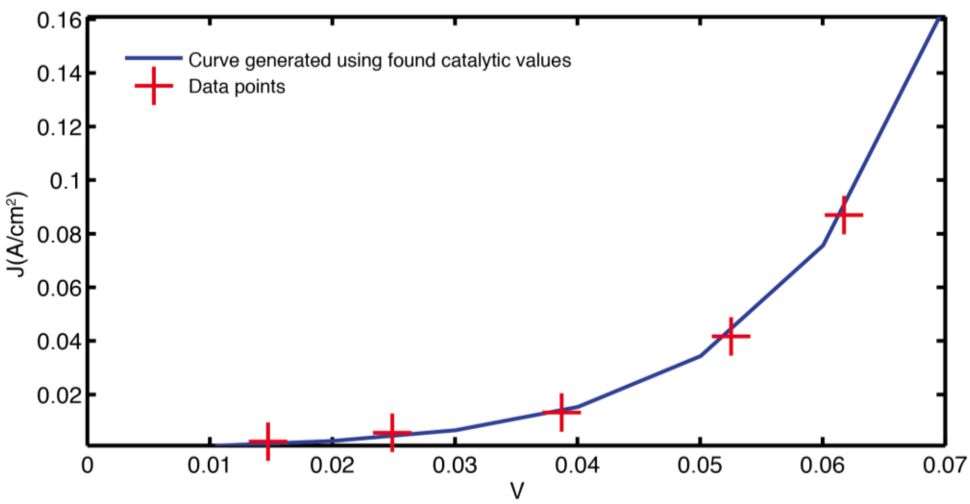

Figure S3: Load curve generated for Platinum using J_0, α values obtained by fitting data points to the Butler-Volmer equation.

The tables below present values used in this study. It is important to point out, that the used values were obtained from empirical fittings to data reported, and any additional physical inference from their magnitude is limited.

Cathodic Materials

Material	α	J_0	Cost ($/g)[4]	Density (g/cm^3)
Platinum	0.0015	0.00072	35.56	21.45
Nickel Molybdenum	0.83	0.014	0.0234	9.60
Nickel	0.76	2.49E-06	0.018	8.59

Anodic Materials

Material	α	J_0	Cost ($/g)[4]	Density (g/cm^3)
Iridium Oxide	0.39	4.89E-10	29.49	11.66
Ruthenium Oxide	0.21	3.03E-08	3.65	6.97
Co_3O_4	0.54	1.05E-09	0.022	8.91

3. Kilograms produced by the system

The operating point of the PV-Electrolyzer was given by the intersection of the PV's output curve and the electrolyzer's load curve. Using the operating current density, the amount of kilograms produced by the system over its lifetime was calculated.

$$Yearly\ production\ of\ H_2 = \sum_{m=1}^{m=12} Days_m \times \sum_{h=0}^{h=24} j_{h,m} \times \frac{0.5\ mol\ of\ H_2}{96500\ C} \times \frac{0.002\ kg}{1\ mol\ of\ H_2} \times 60s \times 60\ min$$

where:

- $Days_m$ = Days in a month.
- $j_{h,m}$ = Operating point j [A/s] at hour h of month m.
- h = hour
- m = month

$$Production\ of\ H_2\ over\ lifetime = Yearly\ production\ of\ H_2 \times lifetime$$

$$Discounted\ Production\ of\ H_2 = Yearly\ production\ of\ H_2 \times \left(\frac{1-(1+R)^{-20}}{1-(1-R)^{-1}}\right)$$

where:

- *r = discounted rate; in this study r=0.20*

4. Cost Function

The cost function is dependent on: the photovoltaic, the amount of electrolyzer material used, the membrane, housing and ancillary component that will hold the system together.

$$Capital\ Cost = \begin{cases} \dfrac{Cost_{PV} + Cost_{Memb} + Cost_{Anode} + Cost_{Cathode} + Cost_{Housing}}{(1+r)^t}, t = 1 \\ \dfrac{Cost_{Memb} + Cost_{anode} + Cost_{cathode}}{(1+r)^t}, t = 5,10,15 \end{cases}$$

$$Cost_{PV} = \frac{\$\ per\ cm2}{kg};$$

$$Cost_{Anode} = \frac{F \times (mass_{anode} \times price_{anode})}{kg};\ mass_{anode} = V_{cat} \times \rho_{anode}$$

$$Cost_{Cathode} = \frac{F \times (mass_{cathode} \times price_{cathode})}{kg};\ mass_{cathode} = V_{cat} \times \rho_{cathode}$$

$$Cost_{Memb} = \frac{F \times \$\ per\ cm2}{kg};$$

$$Cost_{Housing} = F \times Cost_{membrane};$$

and

- F: is the geometrical optimization factor.
- Kg: kilograms produced by the system
- V_{cat}: Volumen occupied by all catalytic material particles.
- $r = discount\ rate$; *in this study r=0.2*

$$Cost_{H_2} = \frac{Capital\ Cost}{Discounted\ Production\ of\ H_2}$$

As explained throughout the study, the factor F being optimized has great impact on the cost of hydrogen. Since cost is dependent both on investment cost and hydrogen production, the figures below explain the relationship of both variables with F. Both graphs also allow explaining with greater detail than image X the existence of an optimal F value as the production curve reaches a plateau around $F=10^{-2}$, while Capital Cost increases with F.

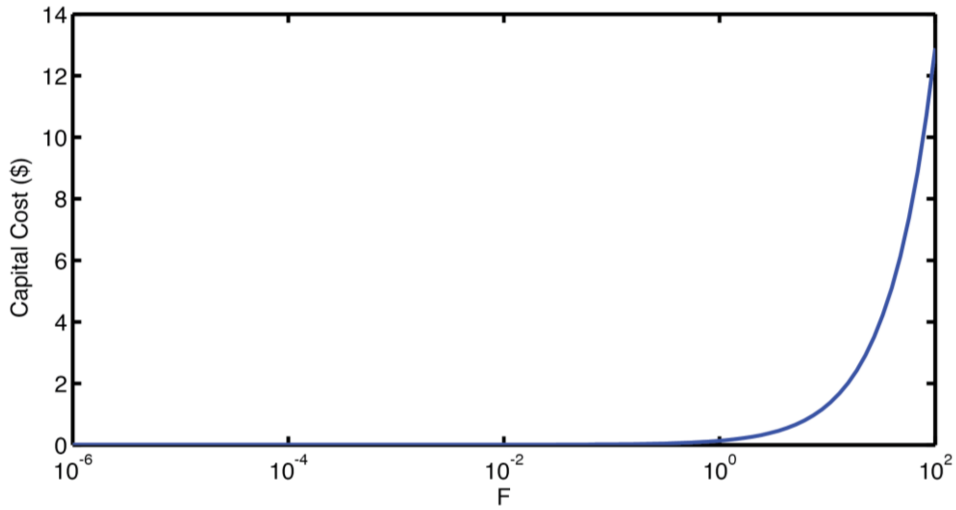

Figure S4: F versus Capital Cost

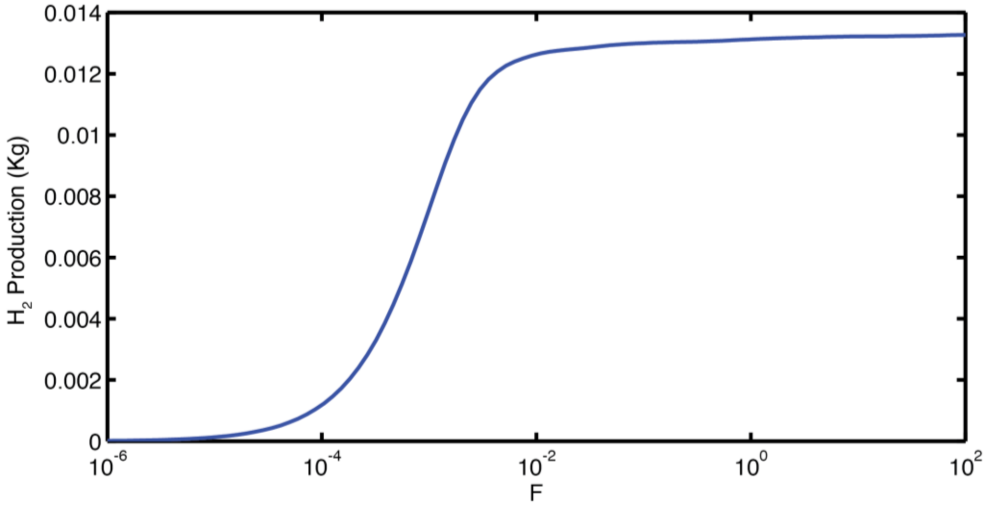

Figure S5: F versus Production of H_2

5. Sensitivity Analysis Parameters

A full factorial sensitivity analysis was performed in this study with the 10 parameters shown below, considering lower and upper bound for each, resulting in 1024 (2^{10}) experiments.

Parameters	Low	High
f_{cat}	0.1	0.9
V_{cat}	4.6e-06	4.6e-05
A_{cat}	55.9	559.4
J_0Cathode (A/cm^2)	4.89e-09	4.89e-11
J_0Anode (A/cm^2)	7.19e-05	0.0079
Cathode Price ($/g)	38.8 [4]	55.4 [4]
Anode Price ($/g)	11.6 [4]	29.5 [4]
PV Cost ($/cm^2)	0.009 [5]	0.02 [6]
Membrane Cost	0.0036 [7]	0.20 [7]

($/cm^2)		
Housing to Membrane Ratio	4.38 [7]	6.18 [7]

Relevant Calculations from table above

- PV's price lower bound

0.84$/W was obtained from IRENA's report[5].

Efficiency of cell was calculated using experimental data provided by CSEM. $\eta = 11.34\%$

$$\frac{0.84\ \$}{W} * \frac{1000W}{m^2} * 0.1134 * \frac{m^2}{(100\ cm)^2} = 0.009072 \frac{\$}{cm^2}$$

6. Study for III-V and crystalline Si cells

For this study, the IV curve for a 26.8% $GaInP_2$/GaAs/Ge photovoltaic was obtained from the SpectroLab's publically available solar cells datasheet [8]. It was assumed that the V_{oc} remains the same for all concentration factors, while the J_{sc} is affected by the concentration factor. The cost per cm^2 of photovoltaic was obtained from a Solar cell generations over 40% efficiency study, and it was of 10$ per cm^2[9].

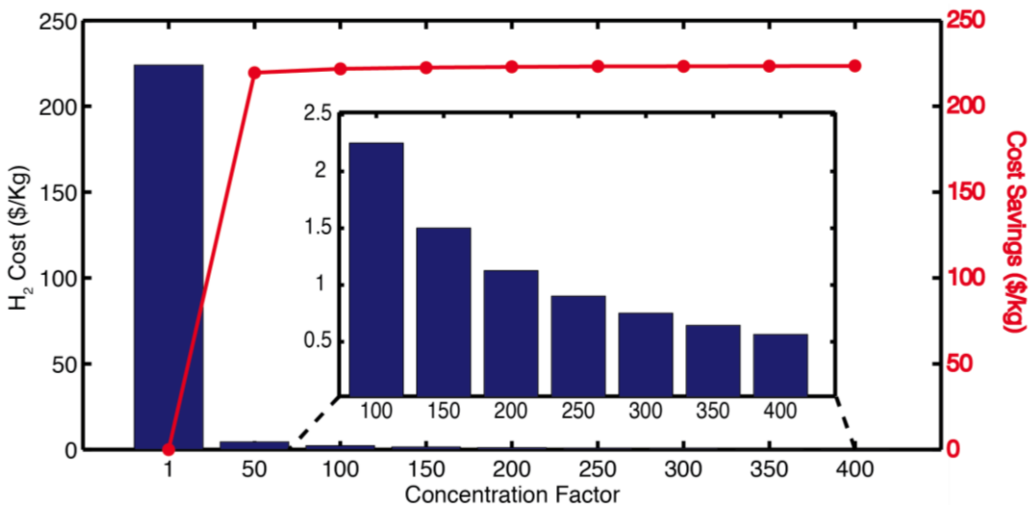

Figure S6: Concentration Study using Spectrolab's 26.8% $GaInP_2$/GaAs/Ge photovoltaic

In the case of crystalline silicon cells, the analysis was performed for a set of cells connected in series in order to achieve enough potential for the water splitting process. The PV data was extracted from the literature.[2] The same geometric optimization used for thin-film Si cells was carried out to obtain optimal F values for the cases of 3- and 4-series connected PV cells, integrated with a Pt/IrO_2 based electrolyzer. The results are shown in the figure below.

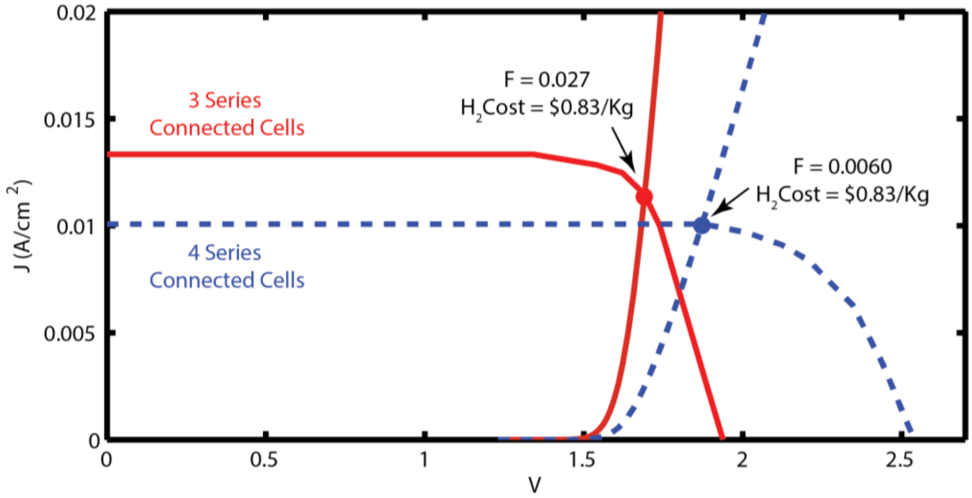

Figure S7: J-V characteristics for optimized solar-hydrogen generators based on crystalline Si PVs, and Pt/IrO2 electrolyzers

7. Comparison between Solar-Electricity and Solar-H_2 production

In order to place our work within the context of clean energy production, the model developed in this study was used to estimate the difference in costs of energy produced by PV panels alone (such as the ones used in this study) and the price of energy stored in fuels using coupled PV-electrolysis systems. The energy produced (in KWh) from PV panels was calculated assuming operation at the maximum power point of the cell described in Figure S1. For the case of PV-Electrolysis systems, the optimized cost for a system based on Pt/IrO_2 catalyst was used. Based on this analysis, the cost of energy for the two systems was compared in $/KWh equivalents, and are presented in the figure below.

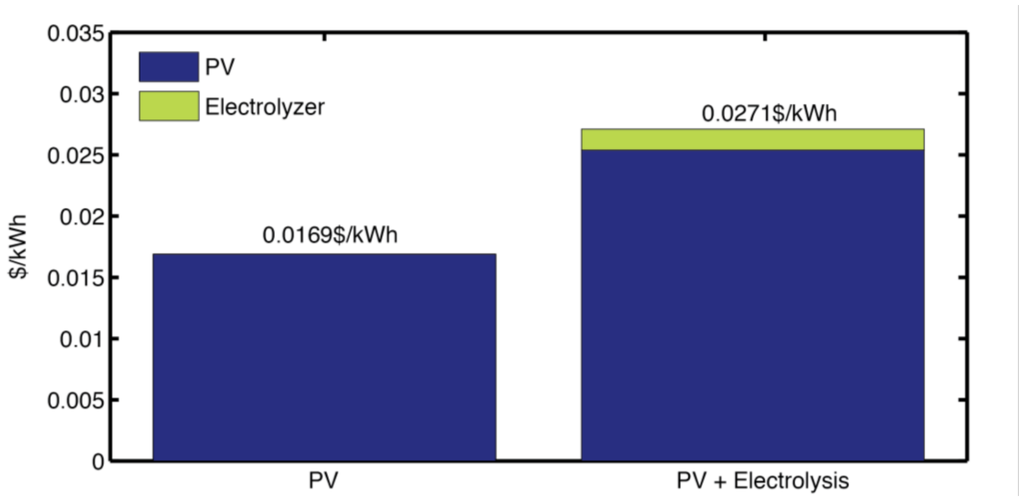

Figure S8: Comparison of energy prices between solar-electricity produced by PV panels, and the price of energy stored in the form of H2 fuel from PV-Electrolysis systems.

The results suggest that the electricity cost from PV panels only (with a cell price of $0.84/W) and irradiation patterns as those implemented in Figure S2 can be as low as $0.0169/KWh (38% lower than the cost of storing energy in the form of H_2). Commercial prices of solar electricity are significantly higher than the cost estimate referred above, which were calculated from only the cost of the PV module. The current levelized cost of solar electricity is estimated at $0.12/KWh by the U.S. Energy Information Agency).[10] Solar electricity costs not only account for the costs associated with the PV module, but also include structural balance of system (BOS), Inverters and AC sub-systems, direct labor, DC electrical losses, Engineering and permissions, inspection and interconnection costs which will yield to cost values that are more realistic for the estimation of commercial prices for solar electricity generation. Values for installed PV modules that include all of these costs vary in the range of 1.77$/W - 3.73$/W, reported in 2014 for utility and residential respectively [11]. Moreover, electricity prices include the cost of transmission and distribution through the grid, which is estimated at ~70% of the cost of electricity generation,[12] but will vary widely depending on the local conditions for the installations. When all of these factors are accounted for, a cost of solar electricity comparable to those reported elsewhere[10] can be obtained.

8. Effects of large variations in electrolyzer systems cost

Given the high uncertainty of the cost of electrolyzer peripheral systems (calculated in basis of housing to membrane costs), the effect of large variations of the MEA housing on the optimal F values, Cost of H_2 and ratio between the costs associated with the electrolyzer and PV were calculated. These results are presented in the graph below (Figure S9). As depicted in the plots, the values of optimized F remain within the same order of magnitude (decreasing by a factor of ~3, while the housing to membrane changes 3 orders of magnitude). The cost of H_2 production changes only slightly, by a factor of ~2 in the 3 orders of magnitude change of the housing pricing. The most significant change is observed in the ratio between the cost carried by the electrolyzer component versus that of the PV. This ratio increases to above 60% when the cost of the housing is raised by 3 orders of magnitude.

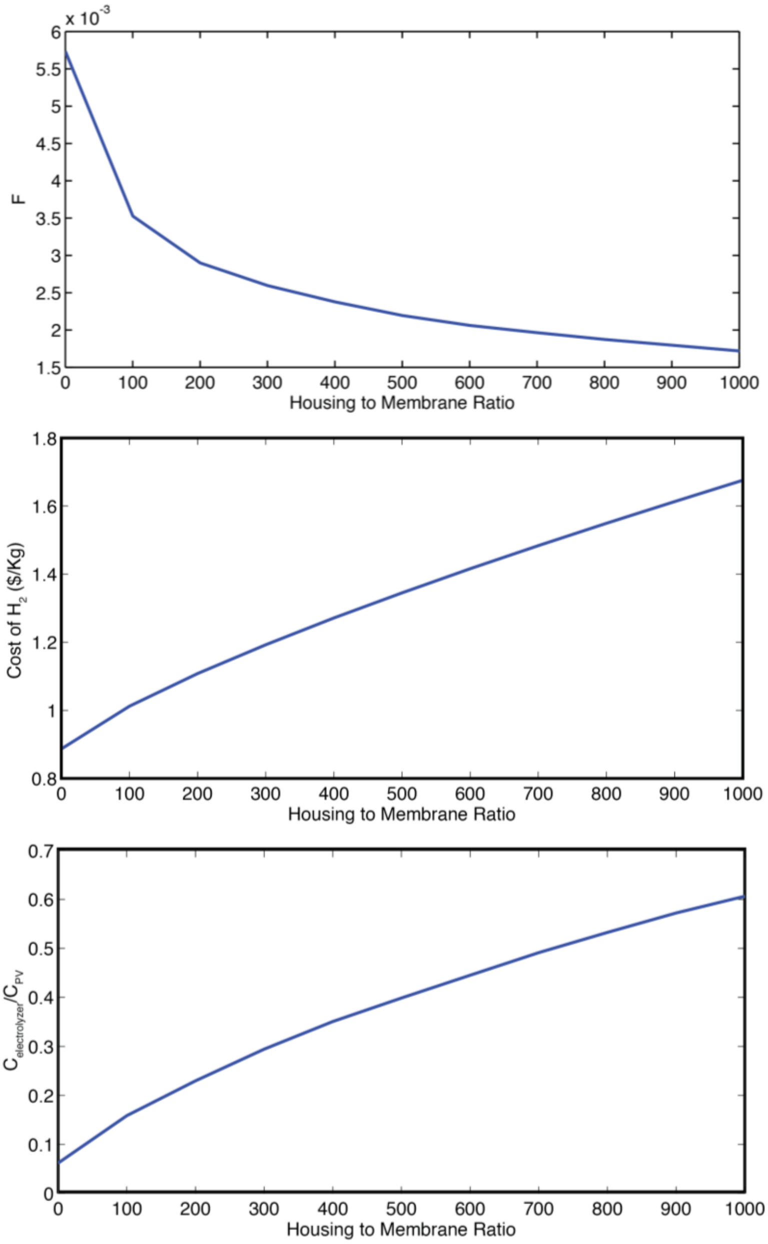

Figure S9: Comparison of energy prices between solar-electricity produced by PV panels, and the price of energy stored in the form of H_2 fuel from PV-Electrolysis systems.

9. Sensitivity of optimal F values on various model parameters

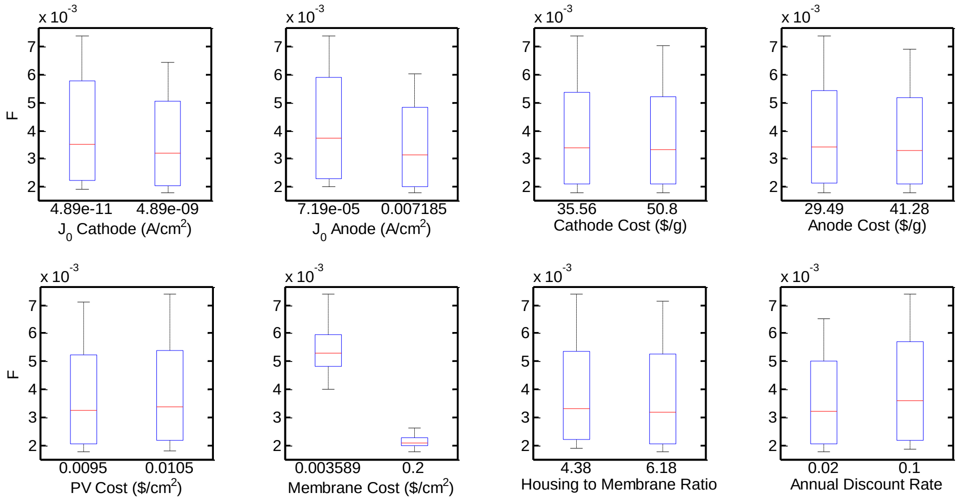

Figure S10: Results from full-factorial sensitivity analysis on various model parameters. In each of the box plots presented above, the red line represents the median of the F value, the blue box covers the area for F values spanning from the first (25%) to the third (75%) quartile, while the dotted bars span values that are within 2.7 standard deviations of the data.

References:

1. Roberts, B., *NREL: Dynamic Maps, GIS Data, and Analysis Tools—Solar Maps.* National Renewable Energy Laboratory, Washington, DC, 2008.
2. Winkler, M.T., et al., *Modeling integrated photovoltaic–electrochemical devices using steady-state equivalent circuits.* Proceedings of the National Academy of Sciences, 2013.
3. Walter, M.G., et al., *Solar water splitting cells.* Chemical reviews, 2010. **110**(11): p. 6446-6473.
4. Survey, U.S.D.o.t.I.a.U.S.G., *Mineral Commodity Summaries 2013.* 2013.
5. Agency, I.R.E., *Renewable Energy Technologies: Cost Analysis Series*, 2012: www.irena.org.
6. Pinaud, B.A., et al., *Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry.* Energy & Environmental Science, 2013. **6**(7): p. 1983-2002.
7. James, B.D. and J.A. Kalinoski, *Mass production cost estimation for direct H2 PEM fuel cell systems for automotive applications.* Status Presentation for Independent Review of the 2008 Cost Estimates, Directed Technologies Inc, 2008.
8. Debe, M.K., *Electrocatalyst approaches and challenges for automotive fuel cells.* Nature, 2012. **486**(7401): p. 43-51.
9. King, R., et al., *Solar cell generations over 40% efficiency.* Progress in Photovoltaics: Research and Applications, 2012. **20**(6): p. 801-815.
10. U.S.EIA, *Levelized Cost and Levelized Avoided Cost of New Generation Resources in the Annual Energy Outlook 2014 (http://www.eia.gov/forecasts/aeo/pdf/electricity_generation.pdf)*, 2014.
11. Greentech Media, I.a.S.E.I.A., *U.S. Solar Market Insight Report Q1 2014 Executive Summary*, 2014.
12. U.S.EIA, *Annual Energy Outlook 2014 (http://www.eia.gov/forecasts/aeo/pdf/tbla8.pdf)*, 2014.