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Performance limits of photoelectrochemical CO₂ reduction based on known electrocatalysts and the case for 2-electron reduction products

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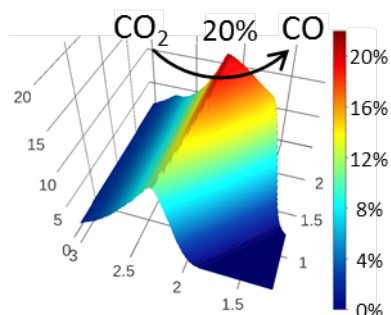
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ABSTRACT

Solar-driven reduction of CO₂ to solar fuels as an alternative to H₂ via water splitting is an intriguing proposition. We model the Solar-To-Fuel (STF) efficiencies using realistic parameters based on recently reported CO₂ reduction catalysts with a high performance tandem photoabsorber structure. CO and formate, which are both 2-electron reduction products, offer surprisingly competitive STF efficiencies (20.0% and 18.8%) very close to solar H₂ (21.8%) despite markedly worse reduction catalysis. The slightly lower efficiency towards carbon products is mainly due to electrolyte resistance – not overpotential. Surprisingly, using a cell design where electrolyte resistance is minimized makes formate the preferred product from an efficiency standpoint (reaching 22.7% STF efficiency). On the other hand, going beyond 2-electron reductions the more highly reduced products seem unviable with presently available electrocatalysts due to excessive overpotentials and poor selectivity. Breaking up the multi-

electron reduction pathway into individually optimized, separate 2-electron steps could be a way forward.

TOC GRAPHICS



The research efforts towards solar fuel synthesis technologies have mostly focused on splitting water into hydrogen (fuel) and an oxygen bi-product. The reasons for this are several: Hydrogen is perhaps the simplest molecule to produce, it has a reasonable free energy content and there exists excellent hydrogen evolution electrocatalysts.^{1,2} It is well known that the optimal configuration for direct photoelectrochemical (PEC³) solar driven water splitting is a two-photon (or “tandem”)-configuration. In a tandem device, two photoabsorbers – each providing photovoltage under illumination, are stacked and series connected such that their combined photovoltage can overcome the thermodynamics of water splitting in addition to all the losses associated with electrochemical overpotentials and resistive losses in the electrolyte and membrane. Both photoabsorbing cells should be designed to evenly split the available solar photons in order to achieve the highest possible photocurrent density while maintaining sufficiently high photovoltage to run the reaction.⁴

Photoelectrochemical water splitting

The specific case of water splitting is covered in both older^{5,6} and more recent literature.⁷⁻¹⁰ Depending on the exact assumptions related to losses, the optimum band gaps for the top- and bottom cells in the tandem are in the range of 1.7 eV – 1.9 eV and 0.95 eV – 1.4 eV respectively;

and the corresponding maximum achievable solar-to-hydrogen (STH) efficiency ¹¹ is in the range of 20% – 29%.

In order to guide the research despite the large gamut of parameters and no obvious “right” set of parameter choices two web-based modelling (WBM) tools have been launched: [SPECDO](#) and [Solarfuelsmodeling](#). SPECDO.epfl.ch, by the Haussener group at EPFL, provides a holistic, systems modeling approach including economics ¹² while Solarfuelsmodeling.com, focusses on the core photoabsorber stack and simulates PEC device thermodynamic performance – not just for water splitting, but for any energy harvesting reaction. ¹³ The WBM software takes a thermodynamic approach based on the diode equation to calculate the IV-behavior of the core photoabsorber stack. This works well for “buried junction” PEC, but it may also be applicable for semiconductor-liquid junction devices, provided a good band alignment between the semiconductor and electrolyte. The analysis presented here was performed using this freely available WBM tool.

Besides the optical aspects of the device and the important compromise of the solar absorber bandgaps, a significant amount of analysis of the engineering and plant design aspects of the cell has appeared in the PEC solar water splitting literature. ^{14–17}

| Photoabsorber parameters | | | Electrochemical parameters | | |
|---|-------|----------------------|--|-----|-----------|
| Temperature | 298 | K | Faradaic efficiency | 100 | % |
| Optical water thickness | 2 | cm | OER onset overpotential (1 mA/cm ²) | 320 | mV |
| Parasitic light loss | 10 | % | OER Tafel slope | 40 | mV/decade |
| Dark saturation current (multiple of theoretical minimum) | 100 | - | Ionic path length | 0.5 | cm |
| Shunt resistance | 10000 | Ω/cm^2 | | | |
| Series resistance | 1 | Ωcm^2 | | | |

Table 1 Standard parameters in common for all simulations presented in this work.

Photoelectrochemical CO₂ reduction

Compared to the analysis carried out for PEC-driven hydrogen production, comparatively little analysis has so far appeared in the literature on other PEC-driven reactions, although a lively debate *pro et contra* water splitting vs. CO₂ reduction is currently ongoing.^{18–20} This is in spite of the fact that a substantial research effort currently devoted to finding electrocatalysts capable of directly reducing CO₂ into energetic compounds such as methane, ethane, and ethanol and, in turn, to integrate such CO₂ reduction catalysts into PEC solar harvesting systems.^{21–24} Only in late 2015 did the first analysis of PEC-driven CO₂ reduction appear.²⁵ In this paper Singh *et al.* modeled single, double and triple junction devices driving various fuel synthesis reactions running at the thermoneutral potential (*i.e.* a hypothetical case). They find that the highest solar harvesting efficiency occurs for CO₂ reduction to CO, and the best configuration is a double junction (tandem) device. It must be emphasized, however, that a simple thermoneutral potential analysis ignores catalytic and ohmic losses, which are unavoidable in any realistic device. Hence Singh *et al.* report a theoretical solar-to-hydrogen (STH) efficiency of 35.4% for a tandem device which, as noted above, is at least 7%_{abs} higher than a careful “best case” analysis⁷ and roughly 15%_{abs} higher than a very careful “realistic case” analysis.¹³ On the other hand, Singh *et al.* also modeled double- and triple junction devices using *experimental* CO₂-reduction current-voltage

data and found that using a copper-based CO₂-reduction catalyst and an IrO₂-based oxygen evolution catalyst it should be possible to directly convert CO₂ and water into a H₂/CH₄ mixture with around 20.3% solar-to-fuel (STF) efficiency. However, it is worth noting, that even in this case hydrogen is still the main product. The non-trivial details of polarization losses and other cell dependent non-idealities have been modelled in detail for PEC-based CO₂ reducing cells.

26,27

Multi-step electrochemical reduction

The reversible potential for converting CO (and H₂O) to any hydrocarbon or oxygenate fuel molecule is lower ($U_{\text{std}} \sim 1000$ mV) than for converting CO₂ to CO ($U_{\text{std}} = 1.33$ V). This means that a mono-functional electrocatalyst which reduces CO₂ step by step (via CO) to *e.g.* CH₄ will have its thermodynamic efficiency limited by the (most) demanding step.

In order for the process to run at the thermodynamic equilibrium potential the system must bind all intermediates *just* right so that every electron transfer step may take place at the equilibrium potential. However, in general, the binding energies of chemically similar intermediates scale linearly with each other on any given site making it impossible for a simple mono-functional electrocatalyst to bind everything just right.^{28–30} As an illustration we consider the reaction $\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_4 + 2 \text{O}_2$, $z=8$, $\Delta G = 817.8$ kJ/mol. All 8 electrons must be supplied at (at least) the reversible potential of the most thermodynamically demanding step for all steps to be downhill. If we assume that the process goes via free CO (as an example) that makes the total energy requirement, $E_{\text{ideal}} = 8 e \times 1.33 \text{ V} = 10.64$ eV, (assuming zero overpotential for the CO step). However, $\Delta G = 817.8$ kJ/mol which only corresponds to $E_{\text{rev}} = 8.48$ eV. Hence even with zero overpotential for both oxygen evolution and for CO₂ reduction such a system would still be

limited to an electrolysis efficiency of $8.48 \text{ eV}/10.64 \text{ eV} = 0.797$ (due to too weak binding of the CO intermediate). The limit for other fuels like ethanol would be similar.

In order to circumvent this limitation, the reduction process may be broken up into (at least) two steps: A first step where CO_2 is reduced to CO, with a reversible thermodynamic potential of $U_{\text{std}} = 1.33 \text{ V}$; and subsequent step(s) where CO is reduced further – in the example to CH_4 , for which $U_{\text{std}} = 0.97 \text{ V}$. In this case, the overall efficiency becomes $(2 \times 1.33 \text{ V} + 6 \times 0.97 \text{ V})/8.48 \text{ V} = 1.0$, *i.e.* there is no fundamental efficiency limitation beyond the practical problems with real-world overpotentials, *etc.*

The benefit of breaking the CO_2 reduction process into a $\text{CO}_2 \rightarrow \text{CO}$ step and a separate $\text{CO} \rightarrow \text{fuel}$ step is not only thermodynamic. It also introduces the option to run the 2-electron steps on different catalysts, in different electrolytes and under different conditions (pressure, pH, temperature, current density, *etc.*). One could even envision a separate process for each 2-electron step – *i.e.* separate electrolyzers/PEC cells for $\text{CO}_2 \rightarrow \text{CO}$, $\text{CO} \rightarrow \text{formaldehyde}$, $\text{formaldehyde} \rightarrow \text{methanol}$, and $\text{methanol} \rightarrow \text{methane}$. For this reason, this work will focus on 2 e^- CO_2 reduction reactions for PEC. The goal here is to model the realistically achievable Solar-To-Fuel (STF)-efficiency for two such reaction products (CO and formate) based on published *experimental* CO_2 -reduction current-voltage data. This entails that we exclusively consider electrocatalysts, which make CO or formate with a high faradaic selectivity (better than 80%) and at reasonable PEC-relevant current densities (at least $10 \text{ mA}/\text{cm}^2$). This rules out many CO_2 reduction catalysts, since they either have poor selectivity or current density.^{31,32}

Photoelectrochemical CO synthesis

We now consider PEC-driven synthesis of carbon monoxide, which is a promising alternative to water splitting. Like H₂, CO is an energetic gaseous compound and an important industrial chemical (in “syngas”).³³ CO, like H₂, is a 2-electron reduction product from its parent compound and on a per electron basis CO (U_{std} = 1.33 V) carries 8% more energy than H₂ (U_{std} = 1.23 V). As a fuel, however, CO is impractical (a poisonous gas with a low gravimetric energy density). Recent research, however, has shown that CO may be further reduced electrochemically to practical liquid fuels such as ethanol.³⁴

The overall reaction is:



In 2012 Chen *et al.* reported that this reaction may run with a faradaic selectivity of almost 100% and at low overpotential on oxide-derived Au.³⁵ At current densities below 2 mA/cm² the measured Tafel slope is only 56 mV/decade. Above 2 mA/cm² mass transport limitations kick in, which gives a higher effective Tafel slope.³⁵ For this reason we consider two different situations based on Chen’s catalyst: One (optimistic) where we assume that clever device design may overcome mass transport issues and simply extrapolate low current behavior (~175 mV overvoltage at 1 mA/cm² and 56 mV/decade Tafel slope). The other (pessimistic), where we use the reported I-V data *as is* – assuming no improvements mass transport. Modestino *et al.* have shown that even modest electrolyte recirculation or agitation may almost eliminate concentration gradients in the electrolyte, so there is hope that the extrapolated case may not be unrealistic in a real device.³⁶ As per our standard conditions (Table 1) we model OER via conservative parameters: (320 mV overpotential at 1 mA/cm² and a Tafel slope of 40 mV/decade) which is easily achieved by existing OER catalysts.^{37–39} We also assume an electrolyte layer above the

device with an optical thickness equivalent to 2 cm of water. For the simulation we further assume a loss of 10% of incident light (reflections, etc.) and that the tandem solar cells are both quite good with a dark saturation current only 100x the theoretical minimum and that shunt or series resistance losses (beyond that of the electrolyte as mentioned above) are almost negligible. These assumptions are consistent with our previous work on water splitting¹³, are deliberately conservative so as to be realizable in practice. The electrolyte reported by Chen *et al.*³⁵ is CO₂ saturated 0.5 M KHCO₃ for which the conductivity is assumed to be 38.8 mS/cm at 298 K and we model ionic resistance with a 0.5 cm effective ionic path length (which is taken to include the resistance of a possible membrane).⁴⁰

The WBM program¹³ finds the photocurrent density for every point on the grid and calculates the STF-efficiency – in this case it is Solar-to-Carbon monoxide – as:

$$STF = 1.33 V \times \frac{\text{photocurrent density}}{\text{incident solar irradiance}}$$

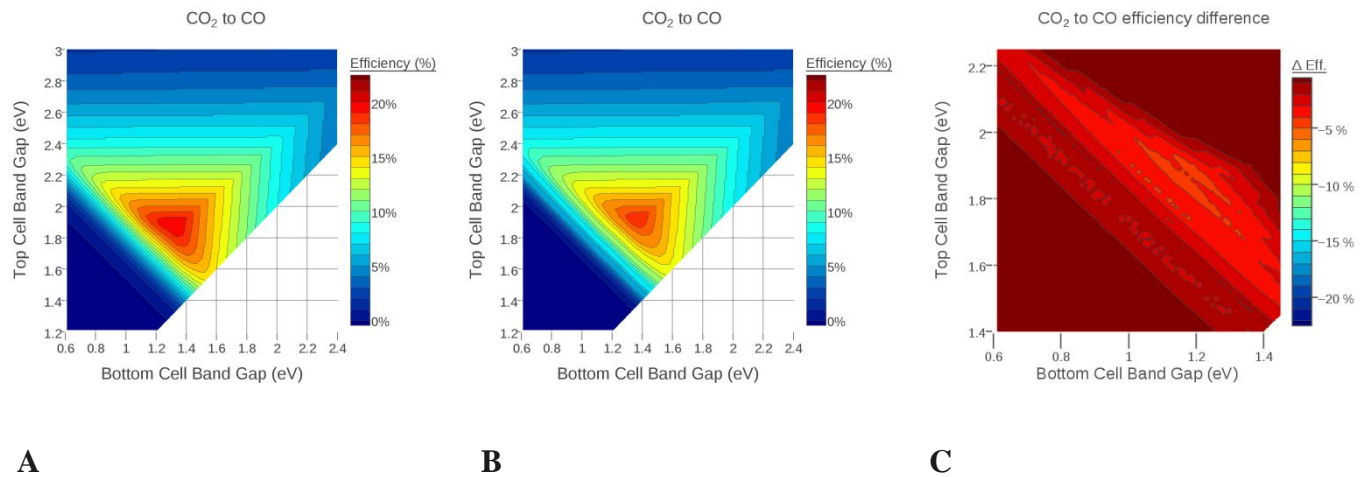


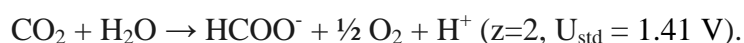
Figure 1 Solar-to-fuel efficiency for CO production as a function of the band gaps of the top and bottom photoabsorber using experimental I-V data for CO₂ reduction³⁵. (A): Extrapolated Tafel CO₂ reduction current (optimistic case). Peak STF efficiency: 20.0% (1.32 eV, 1.89 eV). (B): Raw, as-reported CO₂ reduction I-V data³⁵. Peak STF efficiency:

19.0% (1.38 eV, 1.92 eV). (C): Difference plot (A-B) showing that a maximum STF efficiency loss of 4.5% in the voltage-constrained part of the plot, while near the optimum band-gap range, the loss is only ~1% as indicated in (A) and (B). Standard conditions (Table 1) are assumed. Photon matching of the top- and bottom absorber is assumed.

The results for the two cases are shown in Figure 1. The extrapolated case reaches an ST-CO efficiency of 20.0% while using the raw, measured I-V data³⁵ without extrapolation yields an ST-CO efficiency of 19.0%.

Photoelectrochemical formate/formic acid

Much like CO, formic acid is a useful product which is used industrially to preserve animal feeds and treat leather as well as a chemical feedstock, but it is possible, that it could serve as an intermediate for further reduction to solar fuels in the future. In 2015 Min and Kanan reported efficient reduction of CO₂ to formate over Pd nanoparticles⁴¹, and in early 2016 Gao *et al.* published that a partially oxidized ultrathin cobalt layer may reduce CO₂ to formate at current densities above 10 mA/cm² and with a high faradaic selectivity ~90%.⁴² Since formate seems to be a viable alternative to CO as a 2-electron reduction product, we present the PEC analysis for formate synthesis based on Gao's catalyst here. The reaction in this electrolyte is:



The electrolyte in this case is CO₂ saturated 0.1 M Na₂SO₄ (pH ≈ 6) for which we estimate a conductivity of 18.0 mS/cm at 298 K.⁴⁰ The analysis is conducted by assuming an overvoltage at 1 mA/cm² of 140 mV and a Tafel slope of 44 mV/decade. This is based on slight extrapolation of the reported electrocatalysts performance⁴² to ~14 mA/cm² (experimental data is available up to ~10 mA/cm² so the extrapolation is small) which turns out to be the maximum current relevant

for PEC. We assume that although Gao *et al.* achieved a 90% faradaic efficiency, optimizations should be able to bring this to nearly 100% faradaic efficiency.⁴² The other assumptions about the device are all the same the same as in the CO case. The STF efficiency is calculated as:

$$STF = 1.41 \text{ V} \times \frac{\text{photocurrent density}}{\text{incident solar irradiance}}$$

The result is shown in Figure 2.

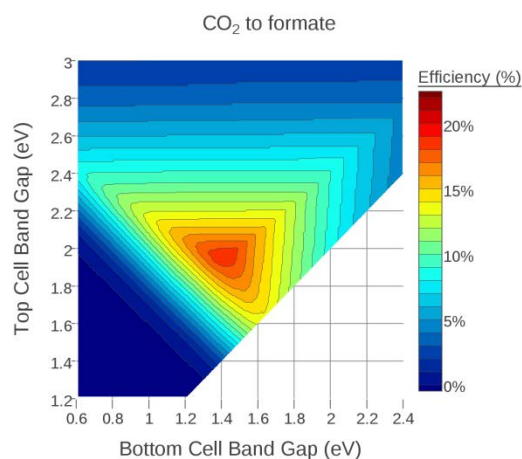


Figure 2 Solar-to-fuel efficiency for CO₂ reduction to formate as a function of the band gaps of the top and bottom photoabsorber using experimental I-V data for CO₂ reduction⁴². Peak STF efficiency: 18.8% (1.42 eV, 1.96 eV). Standard conditions (Table 1) are assumed. Photon matching of the top- and bottom absorber is assumed.

Discussion

The standard conditions in common for all models in this work (Table 1) are chosen by the authors with realism in mind. We note that the STF efficiencies change comparatively little (< 1%_{abs}) upon adjusting any single the parameters within a reasonable range. The exceptions to this (besides the trivial change in STF due to changing the optical light loss or the faradaic efficiency) are: 1) decreasing the shunt resistance or 2) increasing the ionic resistance. A table

showing parameter sensitivities is included in the supplementary material and the WBM tool is freely available on-line to simulate arbitrary parameters.

With the present state-of-the-art catalysts, the three 2-electron products considered (H_2 , CO and HCOOH) all theoretically reach essentially the same maximum PEC-driven STF efficiency limit. *Viz.* for a device design where there is 2 cm of water above the top absorber, but without ohmic losses in the electrolyte, all three reactions may reach a maximum STF efficiency of 22.2% \pm 0.5%, but formate is the winner by a small margin. (STH: 21.8%, ST-CO: 21.8%, ST-Formate: 22.7%) This result is remarkable since the three reactions have different standard potentials (1.23 V, 1.33 V and 1.41 V respectively), in particular since hydrogen evolution over a platinum catalyst has a substantial \sim 180 mV overpotential advantage in comparison to the CO_2 reduction to CO on oxide derived Au and a \sim 130 mV advantage compared to CO_2 reduction to formate over 4-atom Co-layers. The reason that the carbon-containing 2-electron products are competitive from an STF efficiency point of view, despite their significant overpotential disadvantage, is that a tuned tandem system only suffers a minor drop in photocurrent density (from 17.5 mA/cm² to 16.1 mA/cm²) as the operating point is increased from \sim 1660 mV (water splitting) to \sim 1980 mV (formate production). This drop in photocurrent is compensated by the increasing energy content (per electron) of the formate or CO products so the overall result is a similar STF efficiency. In fact, if a CO_2 reduction catalyst existed, which could make either CO or formate at overpotentials similar to HER on Pt (in 2015 such a catalyst was reported for formate⁴¹ and very recently it showed great performance in PEC application⁴³), CO_2 reduction could reach higher STF efficiency than water splitting. This is illustrated in Figure 3, which shows the ideal performance under conditions of zero electrochemical losses, but otherwise

standard conditions (Table 1). Clearly, a tandem absorber system is best suited for operating at a voltage in the 1800 mV – 2400 mV range – *i.e.* where the anode-cathode potential difference under real conditions is in this range. A water splitting cell, which has a realistic operating voltage of ~1660 mV to be delivered by the photoabsorber(s), therefore misses the efficiency peak of a tandem system by about 200 mV whereas CO and formate production operating at 1900 mV to 2000 mV are much closer efficiency peak of a tandem system.

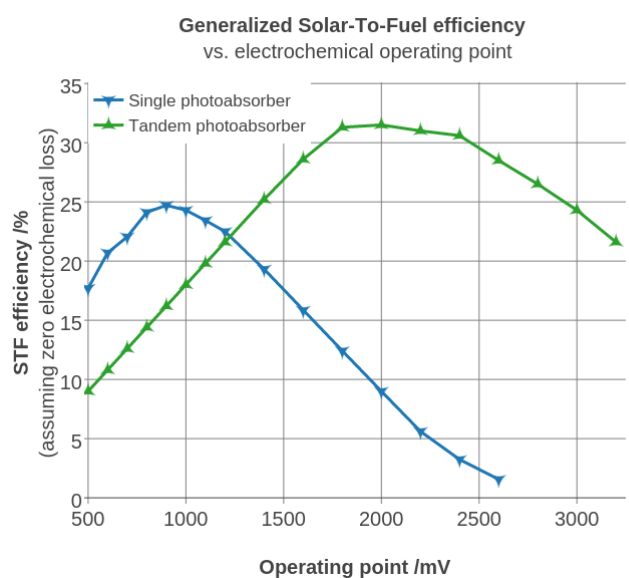


Figure 3 General comparison of maximum Solar-To-Fuel efficiency as a function of the operating point (equilibrium potential) of the device. Electrochemical losses are set to be zero, but otherwise standard conditions (Table 1) are assumed for the photoabsorbers. The operating point for water splitting is ~1660 mV while it is ~1980 mV for formate production.

When ionic losses in the membrane and electrolyte are included (via 0.5 cm of effective electrolyte thickness in the model), as was the cases considered in Figure 1 & Figure 2, the picture becomes more favorable for water splitting because the CO₂ reduction electrolytes have

reduced conductivity compared to the water splitting case. While the water splitting efficiency drops $0.4\%_{\text{abs}}$ due to the addition of ionic resistance voltage loss (maximum STH efficiency of 21.4%), in the ST-CO case the efficiency drops $1.8\%_{\text{abs}}$ to 20.0% (Figure 1), and in the ST-formate case the efficiency drops $3.9\%_{\text{abs}}$ to 18.8% (Figure 2, Figure 4) based on the electrolyte conductances of the reported CO_2 reduction systems.

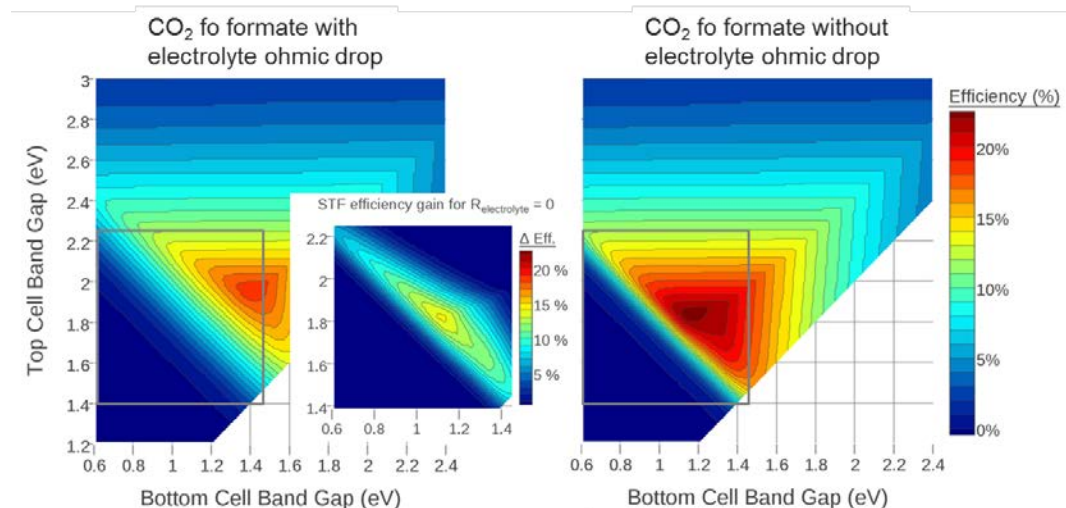


Figure 4 Comparison of solar-to-fuel efficiency for CO_2 reduction to formate comparing the simulated performance including electrolyte potential drop (left) (see also Figure 2 for a clean version of the same graph) with a simulation without electrolyte potential drop (right). The STF efficiency increases from 18.8% to 22.7% at the optimum bandgap combination if electrolyte potential drop is eliminated. The difference plot (center) shows that for a low-bandgap tandem (1.15 eV , 1.8 eV), the STF efficiency gain can be up to $14\%_{\text{abs}}$ by eliminating the electrolyte potential drop. Standard conditions (Table 1) are assumed. Photon matching of the top- and bottom absorber is assumed.

This effect underscores the disadvantage of moderate pH electrolytes and the need for clever device designs, *e.g.* using bipolar membranes^{44,45} to enable use of high ionic strength electrolytes⁴³ and minimize ionic resistance.

Compared to the 2-electron products, all of the more reduced products currently seem impractical to make. The present state-of-the-art copper electrocatalyst can be tweaked to give a combined faradaic yield of C₂-products ethylene, ethanol and ethane (likely via a common acetaldehyde intermediate⁴⁶) of approximately 55%.^{34,47} The low selectivity of Cu and Ag electrocatalysts leave much to be desired.^{48,49} Even using cationic selectivity tuning C₂₊ products make up no more than half the faradaic current⁵⁰, and when the corresponding overpotential of roughly 1000 mV for reasonable current densities is also considered, it becomes clear that the technology to go beyond the 2-electron products is not yet sufficiently mature to be a viable option for a PEC device. For example, if the overall voltage requirement is increased from 2.0 V to 3.0 V the maximum efficiency drops from ~31.5%_{abs} to less than ~24%_{abs} (Figure 3) – *i.e.* a significant 24% relative loss. Clearly, new electrocatalysts with significantly lower overpotential and much higher selectivity are needed in order to make 4e⁻, 8e⁻, and 12e⁻ -solar fuels viable via PEC. The basic problem, however, is that the scaling relations which govern electrochemical CO₂ hydrogenation essentially preclude overpotentials below ~600 mV.^{22,51} The key to more reduced products, therefore, is to find catalysts, which are bi-functional or otherwise may break free of the scaling relations and enable lower overpotentials. PEC-based solar fuel synthesis should become increasingly attractive as improved electrocatalysts hopefully become available in the future, although comprehensive techno-economic analysis similar to what has appeared for solar hydrogen¹⁶ has not yet appeared for PEC-based CO₂ reduction.

At present, PEC-based CO- (or formate) synthesis is very promising since there are good thermodynamic arguments why these products make sense as intermediates in solar fuel synthesis and since selective catalysts for these reactions have appeared in the last few years and

a PEC based formate-producing cell was demonstrated very recently.⁴³ PEC may finally be about other reactions than only water splitting.

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Supplementary information

Parameter sensitivity

| | Optimistic | Standard | Pessimistic |
|---|-------------------------------------|---|-------------------------------------|
| Temperature | 273 K +0.5% | 298K | 323K -0.8% |
| Optical water thickness | 1 cm +0.2% | 2 cm | 3cm -0.1% |
| Dark saturation current (multiple of theoretical minimum) | 10 +0.7% | 100 | 1,000 -1.0% |
| Shunt resistance | 100,000 Ω/cm^2 +0% | 10,000 Ω/cm^2 | 1,000 Ω/cm^2 -1.4% |
| Series resistance | 0.2 Ωcm^2 +0.2% | 1 Ωcm^2 | 5 Ωcm^2 -1.0% |
| | | | |
| OER onset overpotential (1 mA/cm ²) | 280 mV +0.2% | 320 mV | 360 mV -0.3% |
| OER Tafel slope | 30 mV/decade +0.1% | 40 mV/decade | 60 mV/decade -0.2% |
| Ionic path length | 0.25 cm +0.6% | 0.5 cm | 1 cm -1.6% |

Table S1 Sensitivity of the STF efficiency for changes in modelling parameters for CO₂ to CO reduction. The STF efficiency with the standard parameters is 20.0% for this reaction. The change in STF efficiency (in absolute %) is shown when any one of the standard parameters is changed to the values stated.

The change in STF efficiency for with a change of the optical light loss – or the faradaic efficiency is trivial and therefore not included in table S1. As the data in Table S1 shows, improving the tandem solar absorber in terms of shunt resistance or series resistance has very limited benefit, but on the other hand, there is a loss as these parameters worsen. Within a reasonable range, the OER catalysis parameters only affect the STF efficiency moderately, and the same is true for the thickness of the water layer (photons below 1.3 eV aren't absorbed anyway). The conclusion is that effort should be focused on making a good absorber stack and on minimizing the equivalent ionic path length.