Prediction of Limits of Solar-to-Hydrogen Efficiency from Polarization Curves of the Electrochemical Cells

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The maximum solar-to-hydrogen efficiency (STH) in directly coupled photovoltaic-assisted water-splitting systems is achieved when the photovoltaic (PV) and electrochemical (EC) devices are power matched precisely. This matching requires that the polarization curve of the EC device crosses the current–voltage (IV) characteristics of the PV device at its maximum power point (MPP). Conversely, each point on the EC polarization curve can be considered the MPP of a PV device optimally coupled to the EC device. Therefore, at each point on the polarization curve, the minimum PV efficiency and maximum EC efficiency can be calculated for a specific irradiance. The product of both efficiencies generates the STH limit that can be attained at that specific point on the polarization curve. This “reverse analysis,” carried out with elementary math, does not involve any modeling or analysis of PV IV characteristics. Herein, this reverse analysis is described and how it can be used to quantify losses in PV–EC systems and the effect of mutual scaling of PV and EC devices is shown. This method is presented using a NiMo/FeO catalyst pair as an example and was applied to a variety of PV–EC combinations described in the literature.

1. Introduction

Among the various concepts of solar water splitting, photovoltaic-assisted systems combining high-efficiency photovoltaic (PV) devices with electrochemical (EC) cells have potential to provide the highest solar-to-hydrogen efficiencies (STHs).

In particular, efficient photovoltaic-assisted systems are based on the direct connection and optional integration of PV and EC devices.[3–8,10–25] The performance of these PV–EC systems depends on the quality of both the EC and PV components, but also on their power coupling and mutual scaling. Both coupling and scaling are crucial inter-related issues for the minimization of energy losses in the PV–EC system and increasing its STH. Many studies have examined the coupling of various PV and EC devices,[4,10,14,16,18,22,23,26–37] their mutual scaling,[14,15,28,32,38–42] and the limits of STH.[11,21,43–45] In most cases, PV and EC devices are developed separately and then merged at a later stage. To minimize the lab effort and estimate the potential of the PV–EC system in question, prior to hardware integration, it is desirable to determine: 1) the location of the maximum power point (MPP) of the PV device required for optimal matching to the polarization curve of the EC device; 2) the optimal ratio of active areas of the EC and PV devices (AEC/APV); 3) the limit of STH attainable with a given pair of PV and EC devices under a given irradiance.

All three determinations are closely related to the polarization curve of the EC cell. In this work, we show that the polarization curve is sufficient to address these issues even without analyzing the current–voltage (IV) characteristics of a PV device. We begin with the basics of PV–EC operation and a previously reported method[4,10,14,16,18,22,23,26–42] to find the point of optimal coupling for a given polarization curve, PV efficiency, and irradiance. Next, we show how a polarization curve can be transformed to assess STH limits. The transformation method, or “reverse” analysis, is based on the premise that any combination of PV and EC devices achieves maximum STH only when the maximum power of the PV device is delivered to the EC device. For directly coupled PV–EC systems this implies that polarization curve of the EC device crosses the IV characteristics of the PV device at the MPP of the latter device. Hence, in any optimally coupled direct PV–EC system, the MPP of the PV device belongs to the set of points of EC polarization curve. Conversely, each point on the EC polarization curve can be considered the MPP of a hypothetical PV device optimally coupled to the EC device. Once the MPP is known, the efficiency of the PV device can be calculated for a specific irradiance. This is the minimum PV efficiency required to run the EC device at a specific point on its polarization curve. Simultaneously, the voltage efficiency of the EC cell is directly accessible at any point on its polarization curve. The product of both efficiencies gives the maximum or STH limit attainable at a specific point on the polarization curve. This reverse analysis can be performed using absolute currents or area-specific current densities. In the latter case, the impact of the AEC/APV area ratio on the STH limit can be studied to optimize mutual scaling of the PV and EC devices. This method can help to streamline the development of the photovoltaic assisted water splitting systems from the point of view of the EC devices. Via

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simple transformation, the polarization curve of any electrolyzer can be converted to the dependence of the STH limit on the PV efficiency (at assumed irradiance and optionally the $A_{EC}/A_{PV}$ area ratio). Thus, for a given electrolyzer, it is possible to determine the STH limit that can be achieved in combination with any PV device with only the PV efficiency and irradiance known. Furthermore, different electrolyzers can be compared in terms of the STH limit without the need for an actual combination with PV devices or extensive simulations. We show how the results of the reverse analysis can be used to identify and quantify losses in PV–EC systems. In the final part of this study, reverse analysis is applied to characterize some of the PV–EC systems reported in the literature. Throughout this study, the method is presented using polarization curve of an EC cell with NiMo/NiFeO$_x$ catalyst pair.$^{[18]}$

2. Power Coupling in the PV–EC System

A power flow diagram for a PV–EC combination is presented in Figure 1. The light power ($P_{in}$) is converted in the PV device into electric power ($P_{EC}$) delivered to the EC cell, which in turn stores electrical energy into chemical bond energy with power $P_{H2}$.

The solar-to-hydrogen efficiency (STH) of the PV–EC system can be expressed as a ratio of powers, or via the power conversion efficiencies of the system components

$$\text{STH} = \frac{P_{H2}}{P_{in}} = \eta_{PV} C \eta_{EC}$$

(1)

where $\eta_{PV}$ is the PV power conversion efficiency and $\eta_{EC}$ is the power conversion efficiency of the EC device. The PV efficiency $\eta_{PV}$ usually refers to the efficiency at the MPP. The term $C$ is the power coupling factor or “coupling efficiency”$^{[5,22]}$ and is introduced to account for the fact that the working point (WP) of the PV–EC system may deviate from the MPP, causing power mismatch or coupling loss.$^{[21]}$ The coupling problem is illustrated in Figure 2, where an example EC polarization curve is presented together with three example IV characteristics of PV devices with the same conversion efficiency but with different MPP positions.

Although all three PV devices have the same efficiency, only PV2 is optimally coupled to the EC cell in Figure 2 (WP2 coincides with MPP2). Considering PV1 and PV3 in Figure 2, the WPs are off their respective MPPs, which results in significant coupling loss.$^{[21]}$ Provided that a proper electrical connection between the PV and EC devices is established and the resistive loss is negligible—the coupling loss makes up the entire internal loss of the PV–EC system. For the case of optimal coupling with $C = 1$, Equation (1) can be simplified to describe the STH limit in the PV–EC system without internal losses

$$\text{STH}_{\text{limit}} = \frac{P_{MPP}}{P_{in}} = \frac{I_{MPP} V_{MPP}}{P_{in}}$$

(2)

Equation (2) gives the highest STH attainable with a given combination of PV and EC devices, which is the product of their efficiencies. Let us consider the $\eta_{PV}$ and $\eta_{EC}$ terms of product (2) separately.

The PV efficiency ($\eta_{PV}$) is usually expressed as

$$\eta_{PV} = \frac{P_{MP}}{P_{in}} = \frac{I_{MPP} V_{MPP}}{P_{in}}$$

(3)

where $P_{in}$ is the total power of light arriving at the PV device, $P_{MP}$ is the maximum attainable power of the PV device, and $I_{MPP} V_{MPP}$ is the product of current and voltage at the MPP.

The EC efficiency $\eta_{EC}$ is expressed as

$$\eta_{EC} = \frac{P_{H2}}{P_{EC}} = \frac{I_{EC} \Delta E^o}{I_{EC} V} = \frac{\Delta E^o}{V}$$

(4)

where $I_{EC}$ is the working point current, $V$ is the working point voltage, and $\Delta E^o$ is the thermodynamic potential difference of water splitting. Equation (4) describes the voltage efficiency of an EC cell with a Faradaic efficiency of 100%, which is realistic for optimized experimental EC cells.$^{[8,47,48]}$ Although details of the hydrogen and oxygen evolution reactions during water splitting are still under debate,$^{[2,49]}$ we have assumed $\Delta E = 1.23$ V, which is widely used in the literature.$^{[1,6,11,19–23,31–35,43–48,50–55]}$ To calculate the EC voltage efficiency, in this section, we address the coupling and STH limit problems using the absolute currents of both PV and EC devices as well as the absolute total irradiance $P_{in}$, which is practical if both devices have predefined areas. Explicit treatment of the active areas of both PV and EC components is performed in the “Scaling” section.

The point of optimal coupling between a PV device with efficiency $\eta_{PV}$ and an EC cell with a polarization curve $I_{EC}(V)$ can be found using the method reported in the literature.$^{[14,32,46]}$ First, by

Figure 1. Power flow diagram of a PV–EC water-splitting system.
rearranging Equation (3), the dependence of \( I_{\text{MPP}} \) on \( V_{\text{MPP}} \) for a constant \( \eta_{\text{PV}} \) and \( P_{\text{in}} \) can be written as

\[
I_{\text{MPP}}(V_{\text{MPP}}) = \frac{\eta_{\text{PV}} P_{\text{in}}}{V_{\text{MPP}}} \tag{5}
\]

The dependency \( I_{\text{MPP}}(V_{\text{MPP}}) \) is indicated by the red dotted line in Figure 2. The intersection of the \( I_{\text{MPP}}(V_{\text{MPP}}) \) dependence with the polarization curve \( I_{\text{EC}}(V) \) gives the desired \( I_{\text{MPP}} \) and \( V_{\text{MPP}} \) for optimal coupling. Note that, no IV characteristic of the PV device is needed to determine the exact position of the optimal coupling point; only the PV efficiency and total power of light arriving at the PV device \( P_{\text{in}} \) are required. This approach is a practical solution for designing PV–EC combinations; one starts from the EC polarization curve and can approach the most suitable configuration of the PV device. Simultaneously, this approach minimizes the amount of information required to analyze the maximum STH attainable with a given EC cell, which is the focus of our study.

The formal conditions of the intersection between \( I_{\text{MPP}}(V_{\text{MPP}}) \) and \( I_{\text{EC}}(V) \) in Figure 2 are

\[
V_{\text{MPP}} = V \tag{6}
\]

and

\[
I_{\text{MPP}}(V) = I_{\text{EC}}(V) \tag{7}
\]

Using Equations (6) and (7), we can substitute \( V_{\text{MPP}} \) with \( V \) and \( I_{\text{MPP}}(V_{\text{MPP}}) \) with \( I_{\text{EC}}(V) \) in Equation (5) and generate an “optimal coupling equation,” which describes the link between PV output and the EC polarization curve in the optimally coupled PV–EC system, as follows

\[
I_{\text{EC}}(V) = \eta_{\text{PV}} P_{\text{in}} / V \tag{8}
\]

Equation (8) describes the entire set of optimally coupled PV–EC systems built with a particular EC cell; whenever a PV device is optimally coupled to the given EC cell, its MPP belongs on the polarization curve of the EC cell. Conversely, any point on the polarization curve \( I_{\text{EC}}(V) \) is equivalent to the MPP of a PV device optimally coupled to the EC cell.

This principle is illustrated in Figure 3, where the red lines are \( I_{\text{MPP}}(V_{\text{MPP}}) \) dependencies calculated for various \( \eta_{\text{PV}} \). Each \( I_{\text{MPP}}(V_{\text{MPP}}) \) curve represents the set of all possible PV devices with efficiency \( \eta_{\text{PV}} \) under \( P_{\text{in}} = 100 \text{ mW} \). Where the \( I_{\text{MPP}}(V_{\text{MPP}}) \) curves intersect with the \( I_{\text{EC}}(V) \) polarization curve is the point of optimal coupling with a PV device of a given \( \eta_{\text{PV}} \). Therefore, every point of the polarization curve \( I_{\text{EC}}(V) \) is equivalent to the MPP of a PV device optimally coupled to the EC cell.

Finally, at any point on the polarization curve, we can find the minimal efficiency of a PV cell required to run the EC cell at this given current according to Equation (8). This is the first step in approaching the limit in the STH of the entire PV–EC system.

3. STH Limit and Losses in the PV–EC System

The main prerequisite or requirement for maximum efficiency in the PV–EC system is optimal power coupling. Using this requirement together with the equations presented in the previous section, we can calculate the limit of solar-to-hydrogen efficiency (\( \text{STH}_{\text{limit}} \)) for every point on the EC polarization curve. To perform this reverse analysis, we first must determine the minimal PV efficiency required to operate the EC device at a specific point on its polarization curve. A simple rearrangement of the “optimal coupling equation” (8) gives the following expression

\[
\eta_{\text{PV}}(V) = I_{\text{EC}}(V) V / P_{\text{in}} \tag{9}
\]

Note that, there is no upper limit of \( \eta_{\text{PV}} \) in Equation (9) because the nature of the PV device is not considered. Equation (9) gives the lowest PV efficiency sufficient to maintain the required current in the EC cell at a given \( P_{\text{in}} \). Depending on how high the voltage \( (V) \) and respective EC current \( (I_{\text{EC}}) \) are, the required \( \eta_{\text{PV}} \) may exceed any physically reasonable value. The range of applicability of Equation (9) is determined by the range of practically available PV efficiencies.

In the next step, we can find the EC efficiency, which at any point on the EC polarization curve is calculated according to Equation (4) as follows

\[
\eta_{\text{EC}}(V) = \frac{\Delta E}{V} \tag{10}
\]

Finally, by combining Equation (2), (9), and (10), a new expression is obtained for \( \text{STH}_{\text{limit}} \) that is attainable at any point on the EC polarization curve.

\[
\text{STH}_{\text{limit}}(V) = \eta_{\text{PV}}(V) \eta_{\text{EC}}(V) = I_{\text{EC}}(V) \Delta E / P_{\text{in}} \tag{11}
\]

Note that because Equation (11) includes \( \eta_{\text{PV}} \) calculated according to Equation (9), its applicability is also determined by the range of practically available PV efficiencies.
Using Equation (9), (10), and (11), the STH\textsubscript{limit} and losses in the PV–EC system can be calculated using only the polarization curve and \( P_{in} \). Therefore, an assessment of the potential of experimental catalyzer systems for the PV–EC combinations can be simplified, as no details of the PV device are needed. The calculation algorithm is shown in Figure 4.

**Figure 4.** Algorithm for calculation of the minimal PV efficiency (\( \eta_{PV} \)), EC efficiency (\( \eta_{EC} \)), and maximal attainable solar-to-hydrogen efficiency (STH\textsubscript{limit}) as a function of the EC cell operating voltage.

To demonstrate the proposed reverse analysis, we used the polarization curve \( I_{EC}(V) \) of an EC cell with a NiMo/NiFeO\textsubscript{X} catalyst pair reported previously \cite{18} and performed calculations according to the algorithm in Figure 4 using \( \Delta E^\circ = 1.23 \text{ V} \) and \( P_{in} = 100 \text{ mW} \). The polarization curve was scaled by assuming the active area of the EC electrode (\( A_{EC} \)) equals 1 cm\textsuperscript{2}. Note that, the analysis according to Equation (9), (10), and (11) does not require input of device areas because the equations are based on absolute quantities. The effect of the device areas is addressed in the subsequent section. The results of the calculations are presented in Figure 5. Note that, the results in Figure 5 are not universal and are valid only for the specific polarization curve. The results will vary for different polarization curves and irradiance power (\( P_{in} \)) values. The results of the analysis applied to several different polarization curves from the literature are presented at the end of the manuscript in Figure 9.

In Figure 5a, the minimal PV efficiency (\( \eta_{PV} \)), EC efficiency (\( \eta_{EC} \)), and STH\textsubscript{limit} are plotted as a function of the PV–EC voltage (\( V \)), the direct outcome of the calculation. The same data plotted against the \( I_{EC} \), which is common for electrochemistry, are presented in Figure 5b. In both presentations, the same trends were observed. The EC efficiency declines as the voltage and current in the EC cell increase. At the same time, with an increase in \( I_{EC} \), the minimal PV efficiency required to drive the optimally coupled PV–EC system increases, as does the STH\textsubscript{limit}. The increase in STH\textsubscript{limit} was significantly flatter than the increase in PV efficiency in both plots. This is related to the decrease in EC efficiency as the PV–EC voltage increases. In both Figure 5a,b, the difference between \( \eta_{PV} \) and STH\textsubscript{limit} is related to the kinetic loss (overpotential loss) in the EC cell.

From the perspective of PV–EC system development, it is of interest to estimate the maximum STH attainable when the EC device in question is optimally coupled to various PV devices. This information can be visualized by plotting STH\textsubscript{limit} as a
function of $\eta_{\text{PV}}$, as shown in Figure 5c. The black bold line in Figure 5c is the $\text{STH}_{\text{limit}}$ obtainable by the PV–EC system as a function of PV efficiency. The gray diagonal line represents the ideal PV–EC system with no kinetic losses in the EC cell ($\text{STH} = \eta_{\text{PV}}$). The difference between the gray line and $\text{STH}_{\text{limit}}$ represents the losses in the PV–EC system related to the EC cell. The graph in Figure 5c can be used for quick analysis of a PV–EC system in practice.

An example of this analysis is presented in Figure 6, where the dependence from Figure 5 is magnified, and a hypothetical experimental point is included. The point “Measurement” represents a plausible performance of a suboptimally matched PV–EC system with $\eta_{\text{PV}} = 20\%$ and $\text{STH} = 11\%$ under standard test conditions.

The most relevant losses can be identified directly in Figure 6. The horizontal offset between the measured $\eta_{\text{PV}}$ and $\text{STH}_{\text{limit}}$ line is the coupling loss of the PV efficiency, indicated as “PV coupling loss” in Figure 6. This means that an experimental system with nominal $\eta_{\text{PV}} = 20\%$ has the same STH as an optimally coupled system with an $\eta_{\text{PV}}$ of $\approx 16\%$ would have. Because the actual PV output is equivalent to a 16% device, the actual EC overpotential is determined at an $\eta_{\text{PV}}$ of 16%, as shown by the vertical line denoted “EC loss” in Figure 6. The gain in STH attainable in the experimental system via optimized coupling is shown by the blue vertical line “Gain at optimal coupling.” Once coupling in the system is optimized and its STH approaches the $\text{STH}_{\text{limit}}$, the kinetic loss in the system increases and approaches the value indicated by the blue vertical line “EC loss at optimal coupling.” The position of the PV MPP required to bring the experimental system to optimal coupling can be found by solving “optimal coupling equation” (8) graphically, numerically, or analytically depending on how $J_{\text{EC}}(V)$ is specified.

4. Scaling of PV and EC Devices

In the previous section, an example pair of PV and EC devices with fixed areas was analyzed using absolute quantities. In this section, we address the aspect of mutual scaling of the PV and EC devices, which may have a significant impact on the STH and coupling in PV–EC systems.[4,11-13,18,28,32,38-42] As indicated by Chang et al.[32] an increase in the ratio of EC and PV active areas ($A_{\text{EC}}/A_{\text{PV}}$) results in higher STH, but simultaneously requires a higher amount of costly electrolyzer materials and therefore faces economic constraints. To find a proper balance between energy efficiency and system cost, the effect of the $A_{\text{EC}}/A_{\text{PV}}$ ratio on the STH limit must be quantified initially. There is no single definition for the area of a PV cell or module. Different quantities such as “active area,” “aperture area,” and “total area” may be used for the same PV device. Defining the area of an EC device can be even more challenging when catalysts of complex surfaces are used. In both cases, the PV and EC device areas are to a large extent a matter of convention. For the calculations to remain consistent, it is necessary to use the same area to calculate the current densities of the PV and EC devices and calculate the STH limit.

Figure 7 illustrates how variations in PV or EC areas shift the points of optimal coupling in the PV–EC system.

The same polarization curve of the NiMn/CoFeO$_x$ catalyst pair[18] is used in the area-specific form of $J_{\text{EC}}(V)$. The absolute polarization curve scaled with the EC area ($A_{\text{EC}}$) is then $A_{\text{EC}}J_{\text{EC}}(V)$. The two blue curves in Figure 7 represent the polarization curves $A_{\text{EC}}J_{\text{EC}}(V)$ for two EC areas of 1 and 2 cm$^2$. The area of the PV device can be considered by replacing the dependency $I_{\text{MPP}}(V_{\text{MPP}})$ with $A_{\text{PV}}I_{\text{MPP}}(V_{\text{MPP}})$. The dependency $J_{\text{MPP}}(V_{\text{MPP}})$ is calculated using area-specific quantities from the PV efficiency relationship as follows.

![Figure 6](image1.png)

**Figure 6.** $\text{STH}_{\text{limit}}$ plotted as a function of $\eta_{\text{PV}}$. Gray line represents ideal PV–EC device with $\text{STH} = \eta_{\text{PV}}$ data from Figure 5. The point “Measurement” represents the experimental performance of a suboptimally matched PV–EC system with $\eta_{\text{PV}} = 20\%$ and $\text{STH} = 11\%$ under STC.

![Figure 7](image2.png)

**Figure 7.** Blue lines show example polarization curves, $A_{\text{EC}}J_{\text{EC}}(V)$, of an EC cell calculated for the active EC areas of 1 and 2 cm$^2$. Red lines show dependencies, $A_{\text{PV}}J_{\text{MPP}}(V_{\text{MPP}})$, calculated with Equation (13) for $\eta_{\text{PV}} = 20\%$ and standard test conditions of $A_{\text{PV}} = 1$ and 2 cm$^2$. Intersections of $A_{\text{PV}}J_{\text{MPP}}(V_{\text{MPP}})$ and $A_{\text{EC}}J_{\text{EC}}(V)$, representing the points of optimal coupling, are highlighted with yellow circles. The ratio of the active area ($A_{\text{EC}}/A_{\text{PV}}$) is indicated at every optimal coupling point.
\[ \eta_{PV} = \frac{J_{MPP} V_{MPP}}{P_{Din}} \]  

where \( P_{Din} \) is the power density of the light arriving at the PV device, resulting in

\[ J_{MPP}(V_{MPP}) = \frac{\eta_{PV} P_{Din}}{V_{MPP} A_{PV}} = \frac{\eta_{PV} P_{Din}}{V_{MPP}} \]

Two example dependencies \( A_{PV}/MPP(V_{MPP}) \) for an \( A_{PV} \) of 1 and 2 cm\(^2\) are presented in Figure 7 as red curves. The four curves in Figure 7 intersect at four points of optimal coupling, indicated with their respective area ratios \((A_{EC}/A_{PV})\). The positions of these points explain the impact of the \( A_{EC}/A_{PV} \) ratio on the efficiency of the PV–EC system. When the PV area dominates \((A_{EC}/A_{PV} = 1/2)\), the point of optimal coupling shifts to a higher voltage, resulting in reduced EC efficiency. An opposite shift to a higher EC-dominated \( A_{EC}/A_{PV} \) ratio, shifts the point of optimal coupling to lower voltages and higher EC efficiencies. Note that, both points at \( A_{EC}/A_{PV} = 1 \) are at the same voltage, irrespective of the absolute area. Therefore, the ratio of \( A_{EC}/A_{PV} \) areas is the primary parameter for PV–EC optimization. Using area-specific quantities, the optimal coupling Equation (8) can be expressed as

\[ A_{PV} \eta_{PV} P_{Din}/V = A_{EC} \eta_{EC}(V) \]  

The minimal PV efficiency required to operate an EC device at a given point on its polarization curve is expressed as

\[ \eta_{PV}(V) = J_{EC}(V) \frac{A_{EC}}{P_{Din} A_{PV}} \]  

The minimal PV efficiency is directly modulated by the area ratio \((A_{EC}/A_{PV})\). When the area of the EC is increased, the efficiency of the PV device must be proportionally increased to maintain the same current density in the EC cell under the same irradiance.

The EC efficiency equation does not change since it does not include current

\[ \eta_{EC}(V) = \frac{\Delta E^*}{V} \]

Finally, using Equation (2) with Equations (15) and (16), the maximum STH efficiency \((STH_{lim})\) attainable at any point on the EC polarization curve can be expressed as

\[ STH_{lim}(V) = \eta_{PV}(V) \eta_{EC}(V) = J_{EC}(V) \frac{\Delta E^* A_{EC}}{P_{Din} A_{PV}} \]

As well as Equations (9), (11), and (15), the applicability of the calculations according to Equations (15) and (17) is determined by realistically obtainable PV efficiencies. Using Equations (15), (16), and (17), we can repeat the calculations according to the algorithm in Figure 4 for any \( A_{EC}/A_{PV} \). We can calculate \( \eta_{PV}, \eta_{EC} \) and \( STH_{lim} \) as a function of voltage from the same polarization curve\(^{[18]}\) for a wide range of \( A_{EC}/A_{PV} \) ratios. Several \( STH_{lim} \) dependencies on PV efficiency for \( A_{EC}/A_{PV} = 0.1, 1, 10, \) and 100 are presented in Figure 8a. We can see that \( STH_{lim} \) is sensitive to the \( A_{EC}/A_{PV} \) ratio over the entire range of PV efficiencies. At the same time, the absolute gain/loss in \( STH_{lim} \) related to \( A_{EC}/A_{PV} \) is higher at higher \( \eta_{PV} \), as expected. It can also be clearly seen in Figure 8a that when the area ratio is low, even small variations in \( A_{EC}/A_{PV} \) lead to significant shifts in \( STH_{lim} \), whereas the influence is weaker at higher area ratios.

For the optimization of a particular PV–EC combination, it is instructive to estimate how \( STH_{lim} \) depends on the \( A_{EC}/A_{PV} \) at a specific PV efficiency. This dependence is obtained as a vertical slice of the data presented in Figure 8, taken at a specific value of

**Figure 8.** a) Blue lines show dependencies of \( STH_{lim} \) on minimal PV efficiency obtained using Equation (15), (16), and (17) for area ratios of \( A_{EC}/A_{PV} = 0.1, 1, 10, \) and 100. The gray line represents an ideal PV–EC device with \( STH = \eta_{PV} \) as a reference. b) Blue dotted lines show dependencies of \( STH_{lim} \) on the area ratio obtained numerically for \( \eta_{PV} = 10\%, 15\%, 20\%, \) and 25%. The PV efficiencies are shown as horizontal dashed lines for reference.
5. Reverse Analysis Applied to Published Data

The reverse analysis of the STH limit presented in the previous sections can be applied to a variety of reported systems when the polarization curve, PV efficiency, and irradiance are provided. As summarized in Table 1, several literature sources reporting data on PV–EC combinations have been identified that meet these criteria:

We performed calculations according to the algorithm in Figure 4 and obtained the dependencies of STH limit on PV efficiency for the systems reported in the literature. The dependencies are indicated by dotted lines in Figure 9. For clarity, only a portion of each dependency is shown. For every dependency, the point of the actual performance is presented.

In most cases, the STH in each reported system is very close to the STH limit because the systems are optimized for a high degree of power coupling. However, some systems have the potential for gains in efficiency. The overview presented in Figure 9 illustrates how the optimization potential can be assessed with a minimal amount of information and simple math.

6. Discussion

The method of “reverse” analysis can be useful for the rapid design and optimization of PV–EC systems and assessment of their potential. For any electrolyzer, the STH limit can be determined via the simple transformation of its polarization curve. The result of the transformation is the dependence of the STH limit on the PV efficiency at the assumed irradiance level

and optionally, the $A_{EC}/A_{PV}$ area ratio. Thus, the peak performance of the electrolyzer in combination with any PV device can be assessed and, different electrolyzers can be compared in terms of the STH limit. The simplicity of the approach is based on the fact that the STH limit can only be achieved in the optimally coupled PV–EC system, where the PV maximum point belongs on the polarization curve of the EC device. To approach the STH limit in real PV–EC system, the PV device of choice must be precisely matched to the EC device at the target irradiance. The required position of the MPP can be determined by solving Equation (8). Making a PV device with a specific position of the maximum point may be challenging in practice for directly integrated systems. At the cell level, the freedom for multijunction cells exists and at the module level, discrete adjustments of the number of cells or modules in series, together with an optional serial connection of the EC cells, result in a dense grid of possible combinations that very closely approaches maximum efficiency. At the same time, adjustments of the $A_{EC}/A_{PV}$ ratio or adjustments on the side of the EC cell can be used for fine tuning of the power coupling in solar water-splitting systems. Finally, classical MPP tracker solutions allow the PV device to slide along the $I_{MPP}(V_{MPP})$ dependence with a high degree of freedom. However, the latter solution requires modifications to account for losses related to MPP tracking (MPPT) electronics. Thus, a PV device with MPPT can be considered an equivalent PV device with efficiency $\eta_{PV}^\text{M} = \eta_{MPPT} \cdot \eta_{PV}$. The same reverse analysis can be performed for the system with an equivalent PV device with an efficiency of $\eta_{PV}^\text{M}$.

Table 1. PV–EC systems reported in the literature for STH limit evaluation.

| Reference          | $\eta_{PV}$ [%] | STH [%] | $A_{EC}/A_{PV}$ [-] | $P_{MAX}$ [mW cm$^{-2}$] |
|--------------------|-----------------|---------|---------------------|---------------------------|
| Bayrak et al.[22]  | 19              | 12.98   | 1                   | 100                       |
| Chang et al.[6]    | 26.5            | 18.4    | 19.1                | 100                       |
| Heremans et al.[7] | 20.57           | 15.1    | 1.13                | 100                       |
| Jia et al.[7]      | 39.2            | 31.5    | 19.78               | 4200                      |
| Landman et al.[20] | 12.3            | 7.5     | 1                   | 100                       |
| Luo et al.[22]     | 15.7            | 12.3    | 1                   | 100                       |
| Park et al.[9]     | 23.1            | 17.52   | 1                   | 100                       |
| Schüttauf et al.[23]| 20.65          | 14.5    | 1                   | 100                       |
| Shari et al.[18]   | 11.5            | 6.2     | 3                   | 100                       |
| Welter et al.[14]  | 7.7             | 5.1     | 1                   | 100                       |

Figure 9. Reverse analysis with algorithm Figure 4 applied to PV–EC combinations reported in the literature. Dotted lines are the partially presented dependencies of STH on $\eta_{PV}$ for each of the systems. Symbols show the reported points of actual operation. The gray diagonal line represents the ideal PV–EC device with STH = $\eta_{PV}$ as a reference. The literature sources and relevant parameters used for the analysis are summarized in Table 1.
7. Conclusion

In this article, we describe a method to estimate the limit of STH of directly connected PV-assisted EC water-splitting systems (PV–EC systems). The maximum STH is achieved when optimal coupling between the PV and EC devices is achieved. The required point of optimal coupling can be found at the intersection of the EC polarization curve, $I_{EC}(V)$, and the dependence of the maximum power current on the current–voltage characteristics of the PV device. Optimal coupling implies that the MPP of the PV device belongs on the polarization curve of the EC device. In other words, any point on the polarization curve, $I_{EC}(V)$, is equivalent to the MPP of a PV device optimally coupled to this EC cell. Therefore, with known irradiance, three efficiencies can be calculated at every point of the EC polarization curve: 1) the minimal PV efficiency required to run the EC cell at the operating point ($\eta_{PV}$); 2) the voltage efficiency of the EC device itself ($\eta_{EC}$); 3) the STH limit as a product of the PV and EC efficiencies ($\text{STH}_{\text{limit}} = \eta_{PV} \eta_{EC}$).

The current–voltage characteristics of the PV device are not required for this reverse analysis, which simplifies assessment of the potential of EC devices for PV–EC combinations. At the same time, the analysis allows quantification of the coupling loss and overpotential loss in existing PV–EC combinations.

We have shown how to include areas of both devices in the analysis to study the influence of the area ratio $A_{EC}/A_{PV}$ on $\text{STH}_{\text{limit}}$ for further optimization of the system.

The method was presented using the polarization curve of an EC cell with a NiMo/ NiFeO$_x$ catalyst pair as an example.$^{[18]}$ We have also demonstrated how the method can be applied to a variety of systems reported in the literature.

The analysis can be extended to PV–EC systems, including MPP trackers, if related efficiency is considered. Finally, this reverse analysis can be applied to a variety of other EC devices coupled to PVs with necessary adjustments to relevant constants, and in principle, to any load with constant current–voltage characteristics.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

O.A.: conceptualization, investigation, data curation, formal analysis, visualization, writing—original draft, writing—review and editing. V.S.: conceptualization, formal analysis. U.R.: conceptualization, supervision, formal analysis. T.M.: conceptualization, supervision, data curation, formal analysis, writing—review and editing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

photovoltaic electrocatalysts, PV-driven water splitting, solar fuel, solar hydrogen, solar water splitting, solar-to-hydrogen efficiency, water splitting

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