Design Principle and Loss Engineering for Photovoltaic–Electrolysis Cell System

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ABSTRACT: The effects of exchange current density, Tafel slope, system resistance, electrode area, light intensity, and solar cell efficiency were systematically decoupled at the converter-assisted photovoltaic–water electrolysis system. This allows key determinants of overall efficiency to be identified. On the basis of this model, 26.5% single-junction GaAs solar cell was combined with a membrane-electrode-assembled electrolysis cell (EC) using the dc/dc converting technology. As a result, we have achieved a solar-to-hydrogen conversion efficiency of 20.6% on a prototype scale and demonstrated light intensity tracking optimization to maintain high efficiency. We believe that this study will provide design principles for combining solar cells, ECs, and new catalysts and can be generalized to other solar conversion chemical devices while minimizing their power loss during the conversion of electrical energy into fuel.

INTRODUCTION

Splitting water into hydrogen is a prominent pathway for solar energy conversion and storage. The recent development of converting excess electricity into hydrogen supports the advent of the hydrogen economy. Additionally, the hydrogen generated from solar water-splitting reaction shows the possibility to meet the current hydrogen demand. Three different systems have been suggested for using solar energy to convert water into hydrogen. These systems are the photoelectrochemical electrode (PEC), photocatalyst, and photovoltaic–electrolysis cell (PV–EC) systems. Although the state-of-the-art PEC and photocatalyst have 10 and 5% solar-to-hydrogen conversion (STH) efficiency, respectively, a much higher efficiency has been achieved with PV–EC systems. The ease with which the PV–EC systems can be scaled up is regarded to be a great advantage for industrial applications. This superior efficiency can be realized by combining the following two superior pre-existing infrastructures: efficient photovoltaics (PVs) as the power generator and an electrolysis cell (EC) operated at low overpotential for the hydrogen production. Moreover, the compact EC structure fabrication with low electrolyte resistance and finely controlled electrolyte flow for mass transfer limit preclusion are required to maximize the efficiency of the overall system.

The primary requirement for designing an efficient PV–EC system for commercialization is highly efficient and stable photovoltaic (PV) and electrolysis cell (EC) with low overpotential. In the case of the EC system, adoption of efficient water-splitting catalysts and proper cell configuration to minimize the solution resistance and prevent the mass transfer limit at the solution/electrode interface are needed. More importantly, an efficient combination of independent PV and EC systems is also a critical issue for improving the STH efficiency of the PV–EC system. For instance, to use the current close to the short circuit current of PVs, Grätzel group used a NiFe double hydroxide catalyst electrode that has a 16 times larger area than the light-irradiation area on perovskite PVs (15.7% efficiency) and achieved 12.3% STH efficiency, which is equivalent to 78.3% of the PV maximum power. Nocera group highlighted the appropriate number of series-connected Si PVs (16% PV efficiency) on the PV–EC system by comparing the STH efficiency of systems based on three series-connected PVs (2.8%) and four series-connected PVs (10%). Additionally, Fujii group varied the ratio of series-connected ECs and PVs (31.2% of its efficiency) to achieve 24.4% STH efficiency, by consuming 78.2% of the PV-driven maximum power for hydrogen conversion, which is far more efficient than the same number of PVs and ECs connected PV–EC system, with a 14.7% STH efficiency. Recently, by optimizing the electrode area of the EC, solar light density,

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connection methodology, and temperature, Jaramillo group achieved the highest ever STH efficiency (~30%). Although the STH efficiency record has been continuously broken by these pioneering works, it seems that general guidelines to analyze the determinants of each subcompartment in the PV–EC system do not exist. Therefore, further interface engineering and optimization of each compartment can help design a record-high STH-efficient systems.

Here, we conduct a systematic analysis of the PV–EC system to investigate the efficiency determinants by studying models and performing experiments. The decoupled key parameters investigated in our study included the following: (i) existence of a dc/dc converter, (ii) catalyst overpotential, (iii) PV efficiency, (iv) Tafel slope, (v) electrolyte resistance, (vi) surface by modeling, (vii) converter efficiency, (viii) the number of series-connected PVs, and (ix) light intensity. To validate the design principle that we suggested by both modeling and experiments, the decoupled key parameters of catalysts such as Tafel slope and overpotential, size, the scalable and high-performing GaAs PVs can be used as the power supply for designing our PV–EC system. The EC system consisted of IrOx, Pt/C nanocrystalline materials on carbon electrodes and membrane-electrode-assembled (MEA) configuration with low electrolyte resistance. However, the current analysis using these two catalysts can be generalized for use with other cheap and earth-abundant catalysts. Note that the following analyses were made by characterizing the parameters of catalysts such as Tafel slope and overpotential. On the basis of our design principle, we finalized the PV–EC system composed of GaAs PVs, dc/dc converter, and MEA EC. The EC electrode area used in this work was 6 cm², and 40–120 mW of power can be stored as hydrogen energy depending on the PV area (2–6 cm²). The maximum STH efficiency that we achieved by controlling the subcompartments was 20.6%, and 78% of the maximum PV-driven electricity was converted into hydrogen energy. We believe that the new guideline and novel analysis proposed in this work will open up new possibilities not only for analyzing the efficiency of a PV–EC system but also by providing insights into the way PV-Conv-EC systems can be implemented regardless of the PV efficiency, PV and EC connection variation, or catalysts.

### RESULTS AND DISCUSSION

#### Design Principle by Analysis in Terms of Subcomponent Variables of the PV-Conv-EC System

To decouple the determinants of the efficiency of a PV–EC system, the model system with an independent PV and EC governing the
current density–voltage (j–V) equation can be expressed as follows:

\[
\begin{align*}
  j_{\text{PV}} &= j_{\text{EC}} - j_0 \left[ q (V_{\text{PV}} + j_{\text{PV}} R_d) / n k T - 1 \right] \\
  &\quad - (V_{\text{PV}} + j_{\text{PV}} R_d) / R_d \quad (1) \\
  V_{\text{EC}} &= V_0 + \tau_{\text{cat}} \log \left( j_{\text{EC}} / j_{0,\text{cat}} \right) + \tau_{\text{ano}} \log \left( j_{\text{EC}} / j_{0,\text{ano}} \right) \\
  &\quad + j_{\text{EC}} R_{\text{sol}} \quad (2)
\end{align*}
\]

Equation 1 is the diode equation of PV materials consisting of a short circuit current density (j_{sc}), dark current density (j_0), charge of electron (q), series resistance (R_i), ideal diode factor (n), ideal gas constant (k), temperature (T), shunt resistance (R_{Sh}), photogenerated voltage (V_{PV}), and current density (j_{PV}).

Equation 2 is the EC j–V relationship consisting of thermodynamic water electrolysis potential (V_{\text{ff}} 1.23 V at 298 K), Tafel slope of the cathode and the anode (\tau_{\text{cat}} and \tau_{\text{ano}} respectively), exchange current density of the cathode and the anode (j_{0,\text{cat}} and j_{0,\text{ano}}), solution resistance (R_{\text{sol}}), applied voltage on EC (V_{\text{EC}}), and current at EC (j_{\text{EC}}). The EC electrode and light irradiance area to the PV are regarded as the same unless otherwise stated. Moreover, in eq 2, the total overpotential of the EC catalysts for reaching 10 mA cm^{-2} is negligible compared with water-splitting reaction.

Thus, we assume that the faradaic efficiency (\eta_{\text{EC}}) was 1, 18.5 mW cm^{-2} of \text{H}_2 was generated, and 5.3 mW cm^{-2} of \text{P} was wasted. However, the PV–EC operating power (p_{\text{PV},\text{max}} 29 mW cm^{-2}) is always lower than the maximum power of PV (p_{\text{PV},\text{max}} 29 mW cm^{-2}), as shown in Figure 1a. The discrepancy between the p_{\text{PV},\text{max}} point and high p_{\text{H}_2} point is due to the current density–voltage coupling. If it is possible to make the EC use p_{\text{PV},\text{max}} regardless of the intersection current by decoupling the current–voltage of the PV and EC, a higher p_{\text{H}_2} can be achieved.

To resolve the limitation of current density–voltage coupling between PV and EC, we propose a second model system that represents the PV–EC system with a (i) dc/dc converter. PV-linked converter application is a well-known method to help electrical power consumption devices to use the maximum electrical power of PVs.\textsuperscript{24–26} Therefore, the converter application allows p_{\text{PV},\text{max}} to be consumed on the EC by converting PV voltage and current density at p_{\text{PV},\text{max}} point into voltage and current density following the EC j–V relationship, called the “maximum power point tracking” (MPPT). In this modeling, we assume that the converter efficiency is 100\%, indicating that the power generated by the solar cell can be fully consumed by the EC without power loss. Comparison of the MPPT process with the previous model is displayed in Figure 1b, which is equivalent to the PV-Conv-EC system model assuming that no power loss occurs during the converter application. Compared with p_{\text{H}_2} in Figure 1a (18.5 mW cm^{-2}), the MPPT process on the PV–EC system shows higher p_{\text{H}_2} gain (22 mW cm^{-2}), indicating that 3.5 mW cm^{-2} of extra p_{\text{H}_2} can be additionally stored. Although 7 mW cm^{-2} of p_{\text{H}_2} exists even after using the converter, the total loss of the PV-Conv-EC system is far lower than that of the converter-unassisted model, with 10.5 mW cm^{-2} of electrical power loss. Additionally, the converter application can always ensure maximum power utilization generated from the solar cell regardless of the light intensity, which will be further discussed later.

To analytically investigate the effect of the catalyst performance on the PV-Conv-EC system, the amount of p_{\text{H}_2} was determined along with the (ii) catalyst overpotential parameter (\eta_{\text{10mA}}) at (iii) various PV efficiencies. Figure 1c describes the p_{\text{H}_2} gain by the PV-Conv-EC system with different subcompartment applications; in this work, two \eta_{\text{10mA}} (300 and 600 mV) and three PVs with different efficiencies (10, 20, and 30\%) are selected as independent EC catalysts and PV performance descriptors, respectively; especially, the 300 mV of \eta_{\text{10mA}} can be almost achieved even with the transition-metal-based catalyst materials such as NiCeO\textsubscript{2} water oxidation and NiMo water reduction catalysts with 280 and 40 mV overpotential reaching 10 mA cm^{-2}, respectively.\textsuperscript{27,28} Solar cells with 10, 20, and 30\% efficiency were modeled based on the representative examples such as a series-connected organic solar cell, perovskite solar cell, and GaAs solar cell, respectively.\textsuperscript{23,29,30} The j–V curves of PVs are shown in Figure S1. At each p_{\text{H}_2} gain, the extra p_{\text{H}_2} is denoted as the check patterns in Figure 1c to indicate the amount of additional p_{\text{H}_2} gain after the converter application on the PV–EC system. Thus, p_{\text{H}_2} region except for the extra p_{\text{H}_2} is identical to the p_{\text{H}_2} gain by the PV–EC system without the converter application. Focusing that the p_{\text{H}_2} with the PV–EC system without the converter is almost consistent despite catalysts with different \eta_{\text{10mA}} utilization, the converter application is an indispensable factor to thoroughly receive benefits of low
overpotential catalysts. Taking into account the importance of the converter application, we compare the $P_{H_2}$ gain of the PV-Conv-EC system at each independently varied PV and EC performance parameters. The highest $P_{H_2}$ gain (23 mW cm$^{-2}$) is observed for the PV-Conv-EC system in combination with PV with the highest electrical conversion efficiency (30%) and the lowest catalyst $\eta_{10mA}$ (300 mV). With the same PV utilization, however, the $P_{H_2}$ is only 19.4 mW cm$^{-2}$ when a catalyst with relatively higher $\eta_{10mA}$ (600 mV) was used. This indicates that 3.6 mW cm$^{-2}$ of additional $P_{H_2}$ can be achieved by improving the performance of the catalysts. By contrast, in the case of 10% PV, only 1.3 mW cm$^{-2}$ of additional $P_{H_2}$ gain is achieved when lower overpotential catalysts are used. Considering that the additional $P_{H_2}$ by catalyst utilization with low overpotential at 30% PV is approximately threefold higher than that with 10% PV, the dominance of catalyst overpotential becomes more firmly established with highly efficient PV utilization by the PV-Conv-EC system.

The $P_{H_2}$ variation can be further extended in terms of specific EC catalyst parameters such as the summation of (iv) the Tafel slope of the catalysts ($\tau_{cat} + \tau_{ano}$) and $\eta_{10mA}$ based on eqs 2 and 3, as shown in Figure 1d. Although $P_{H_2}$ gains by both PV–EC and PV-Conv-EC systems are highly dependent on $\eta_{10mA}$, the $P_{H_2}$ profiles along the varied catalyst $\eta_{10mA}$ are different. For instance, $P_{H_2}$ at PV–EC without the converter was almost constant when $\eta_{10mA}$ is lower than 700 mV and started to decrease abruptly when $\eta_{10mA}$ exceeded 700 mV. By contrast, instead of an abrupt $P_{H_2}$ decrease, a gradual decrease in $P_{H_2}$ is observed at the PV-Conv-EC system. Furthermore, compared with the PV–EC system, $P_{H_2}$ of the PV-Conv-EC system is dependent more on $\tau_{cat} + \tau_{ano}$ at a low $\eta_{10mA}$. For instance, under a fixed $\eta_{10mA}$ (300 mV), consistent $P_{H_2}$ was kept at 18.5 mW cm$^{-2}$ with the PV–EC system without the converter application. By contrast, 22.6 mW cm$^{-2}$ of $P_{H_2}$ can be increased to 23 mW cm$^{-2}$ when a catalyst with 90 mV dec$^{-1}$ of $\tau_{cat} + \tau_{ano}$ was instead used with catalyst with 200 mV dec$^{-1}$ at the PV-Conv-EC system. We also found that the decrease in $\tau_{cat} + \tau_{ano}$ remarkably fosters $P_{H_2}$ to increase when catalysts with lower $\eta_{10mA}$ are used. This is because relatively small $P_{H_2}$ increase was observed with a decrease in the Tafel slope at a high overpotential such as $P_{H_2}$ increased from 16.2 to 16.3 mW cm$^{-2}$ when the $\tau_{cat} + \tau_{ano}$ was decreased from 200 to 90 mV dec$^{-1}$ at an $\eta_{10mA}$ of 1000 mV. Considering that $P_{H_2}$ increase was more than 0.4 mW cm$^{-2}$ because of the decrease in the Tafel slope at 300 mV of $\eta_{10mA}$ a relatively small amount of additional $P_{H_2}$ (0.1 mW cm$^{-2}$) was obtained with the catalysts with 1000 mV of $\eta_{10mA}$. This case study shows that the $\tau_{cat} + \tau_{ano}$ decrease can help the PV-Conv-EC system to take advantage of high $P_{H_2}$, particularly using catalysts with a low overpotential. From the results shown in Figure 1c,d, we can conclude that high $P_{H_2}$ (23 mW cm$^{-2}$) gain is achieved with the catalysts with low $\tau_{cat} + \tau_{ano}$ (90 mV dec$^{-1}$) and $\eta_{10mA}$ (300 mV) parameters and that are identical to 77% power of $p_{PV,max}$ (30 mW cm$^{-2}$), far higher than 60% $p_{PV,max}$ to $P_{H_2}$ ratio with the conventional PV–EC system.

Even if efficient catalysts with low overpotential and Tafel slopes are used on the EC, (v) solution resistance of the EC can be affected by the $P_{H_2}$ value based on the solution resistance term in eq 2. Additionally, in a practical situation, it is possible to control (vi) the EC to PV surface area ratio. This control can alter the current-related constant such as the ratio among $j_{EC}/j_{0cat}$ and $j_{0ano}$, triggering $P_{H_2}$ to be varied in return. Figure S2 shows the $P_{H_2}$ variation in terms of solution resistance and $A_{EC}/A_{PV}$ ratio to analyze their dominancy. In real situations, many variables related to the catalyst or solar cell will not exactly follow the relationship that we verified in Figure S2. However, Figure S2 tells us that an efficient and a low-cost EC catalyst should be used for the PV-Conv-EC system for effectively increasing $P_{H_2}$ instead of increasing the EC electrode surface area. The low resistance and high $A_{EC}/A_{PV}$ configuration guarantee a higher $P_{H_2}$ gain with the PV-Conv-EC system in terms of light-irradiation area on PVs. In this regard, MEA EC configuration perfectly matched this requirement because of the thin membrane that helps to minimize the electrolyte resistance and to control the EC electrode area by simply preparing an optimal area of supporting electrodes and membranes.

Scheme 1 indicates the schematic of the PV-Conv-EC system composed of independent devices to meet all requirements suggested from Figures 1 and S2. To be specific, series-connected GaAs PV modules, buck-type dc/dc converter, and MEA ECs are consecutively linked using wires. In addition to the low resistance and feasibility to control the $A_{EC}/A_{PV}$ ratio, the MEA configuration of the EC also warrants high purity of hydrogen and low resistance because of the existence of thin proton exchange membrane.

Improving Design Principle by Implementing the PV-Conv-EC System. For implementing the PV-Conv-EC system, we assembled the EC and verified its performance in terms of parameters derived from catalyst materials, system configuration, and product purity (Figure 2). To be specific, IrO$_x$ and Pt/C nanocrytallines were used as water oxidation and reduction catalysts (Figure S3). On the basis of this catalytic property of materials, the Tafel slope and overpotential of the catalytic material were analyzed by converting the j–V curve into an overpotential–log j curve (Figure 2a). We specify the log j range of 0.9–1.3 to purely analyze the water-splitting reaction of our catalysts without the charging effect. The slope of the overpotential–log j curve of each catalyst corresponds to the Tafel slope. Moreover, after combining catalyst electrodes into an EC, the performance of EC can be overlaid on the overpotential–log j slope after iR compensation process by resistance derived from Figure S4. The slope (98 mV dec$^{-1}$) for increasing 1 order of current density at the EC was perfectly consistent with the summation of the Tafel slope of the cathode (32 mV dec$^{-1}$) and anode (66 mV dec$^{-1}$) electrodes. Furthermore, the overpotential for reaching 10 mA cm$^{-2}$ (300 mV) was also identical to the summation of the cathode
The electrical activity of the PV-Conv-EC system can also be illustrated as equivalent circuits (Figure 3a). Compared with conventional PV–EC system circuits, which are identical to the combination of independent PV and EC circuits, a converter between independent systems is the distinguished feature of the PV-Conv-EC system circuit. The resistance and capacitor at each EC electrode represent power consumption due to the water-splitting reaction and the charging effect caused by the electrodes. The PV circuit contains shunt and series resistance. In the case of the converter circuit, the degree of switch (S1) on/off ratio, called the “duty ratio”, and the inductor help the EC to use the maximum power of the solar cell \((P_{PV,\text{max}})\) regardless of the current–voltage coupling. When \(S_1\) is off, \(S_2\) is automatically turned on to operate its circuit. In our case, the buck-type converter is used, and this helps decrease the voltage to be applied to the EC compared with the voltage at the PV. Despite the decreased voltage at the EC, the current on EC is far higher than the photogenerated current in return. Additionally, based on the fact that the average voltage gain at the power-consuming part is identical to the photogenerated voltage, multiplying it with the duty ratio of the converter, theoretical input duty ratio is determined to be \(V_{EC}/V_{PV}\), where the power generated by the PV at \(V_{PV}\) and the power consumed by the EC at \(V_{EC}\) are equivalent. Altogether, to use the \(P_{PV,\text{max}}\) at the EC compartment, the duty ratio for the MPPT process should be predicted as \(V_{EC,\text{MPPT}}/V_{PV,\text{max}}\) where \(V_{PV,\text{max}}\) and \(V_{EC,\text{MPPT}}\) indicate the \(P_{PV,\text{max}}\) voltage and the voltage that was applied to the EC to consume the \(P_{PV,\text{max}}\) respectively. In addition, the converter circuit has complementary metal–oxide–semiconductor (CMOS), it is unable to escape from power loss during the conversion process. Power losses in CMOS circuits include the conduction loss caused by the parasitic resistance and the switching loss attributed to the switching operation of the metal oxide semiconductor field effect transistors (MOSFETs). Thus, even with the MPPT process, \(\eta_{\text{conv}}P_{PV,\text{max}}(\eta_{\text{conv}} < 1, \eta_{\text{conv}} = \text{converter efficiency})\) of power is used by the EC to generate hydrogen. With the independent PV and EC performance parameter, \(P_{H2}\) at the implemented PV-Conv-EC system can be predicted (Figure 3b). The \(I–V\) curve of the series-connected GaAs PVS is shown in Figure S7. STH efficiency can be derived from \(P_{H2}\) from overlaid graphs by the following equation

\[
\text{STH} = \frac{P_{H2}}{n \times (236{,}000 \text{ J/mol}) \times [A_{PV} \times \text{p_{xal}}]} \times \eta_{f} \times \eta_{\text{EC}} \times \eta_{H2} \times \eta_{p_{xal}}
\]

Although the original STH efficiency is expressed in terms of hydrogen evolution rates \((n)\) and its free energy \((236{,}000 \text{ J mol}^{-1})\) divided by \(A_{PV}\) and light density \((p_{xal})\), the numerator of the equation can be converted into current measured on the EC compartment \(I_{EC}\), 1.23 V, and \(\eta_{f}\) at the EC. We assume that the converter can transfer the full amount of the PV-generated power to the EC. Through calculation, STH efficiencies can be estimated to be 21.5% \((17.52 \text{ mA cm}^{-2})\), 1009–1018

![Figure 2. Electrochemical analysis of the electrode material and the MEA EC. (a) Tafel slope of each cathode and anode and the MEA EC system. The sum of the Tafel slope and the overpotential of each electrode is similar to the MEA EC. (b) j–V curve of the MEA EC at different electrolyte resistances controlled by the distance between the cathode and anode. The inset displays the similarity of the j–V curve at each resistance after iR compensation.

(30 mV) and anode (270 mV) overpotentials. Altogether, it is valid that no parasitic current is generated after implementing the EC with both catalyst materials. Seemingly, we can predict the final \(p_{H2}\) with the given catalyst performance thanks to the proposed design principle as suggested above.

To better achieve low resistance on the EC, MEA configuration was implemented with nanocrystalline catalyst decoration on its electrode. In MEA cell with 6 cm² of electrode area, proper distance between electrodes should be used to minimize the electrolyte resistance and product separation. Because the electrolyte resistance is in proportion to the distance between the cathode and anode electrodes, distance between the electrodes was controlled by Nafion thickness. The electrolyte resistance decreased as the thin membrane was assembled (Figure S4b). Thus, the MEA EC with low resistance guarantees higher current density at the same applied voltage (Figure 2b). Considering that the \(j–V\) performance after solution resistance compensation is similar regardless of the electrolyte resistance, it is plausibly attributed to an identical catalytic performance even under different electrode distances. Additionally, \(\eta_{f}\) was measured at each MEA EC (Figure S5). Regardless of the distance between electrodes in the EC, \(H_2\) faradaic efficiency \((\eta_{f})\) was almost 100%. To be specific, the EC with 2.1 \(\Omega\ cm²\) of resistance showed 99.6% of \(\eta_{f}\) indicating that even the MEA EC with the lowest electrolyte can guarantee pure hydrogen collection without hydrogen crossover into the anode compartment. The minimal amount of \(O_2\) \((0.2\% \text{ of produced } H_2\) at 120 s) at the cathode compartment also supports this. Instead, \(O_2\) existed in the anode chamber \((\eta_{f} = 89\%\) of the EC (Figure S6). Because an EC with the lowest resistance guarantees purified \(H_2\) storage and \(\eta_{f}\), we applied the EC with the lowest resistance to PV-Conv-EC connection. DOI: 10.1021/acsomega.7b00012

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20.9% (17.03 mA cm\(^{-2}\)), and 20.6% (16.78 mA cm\(^{-2}\)) when \(A_{\text{EC}}/A_{\text{PV}}\) ratios were 3, 1.5, and 1, respectively. As calculated in Figure 2d, 0.996 of \(\eta_d\) was used for STH prediction. Additionally, based on the overlaid power \((P)\)−\(V\) curve in Figure 3b, the theoretical duty for the MPPT \((D^3)\) as we mentioned previously was expected to be 0.84, 0.85, and 0.87 at each configuration when \(A_{\text{EC}}/A_{\text{PV}}\) ratios were 3, 1.5, and 1, respectively. Without the converter application, only 18.4% STH efficiency can be estimated because of the voltage−current coupling at all configurations. By connecting the independent PV, converter, and EC, as shown in Scheme 1, we can generate and collect hydrogen (Figure S8). In this system, the STH efficiency can be converted from \(I_{\text{EC}}\) measured by potentiostat as an ammeter (Figure 3c). In a practical situation, the optimized input duty for MPPT \((D^3)\) during the PV-Conv-EC operation was not identical to the \(D^3\) predicted from Figure 3b. Therefore, an extra procedure for determining the \(D^3\) for each configuration is necessary. The MPPT process in the experiment was conducted by deciding whether \(P_{\text{PV, max}}\) and measured power \((I_{\text{PV}} \times V_{\text{PV}})\) at the PV compartment were identical during the system operation. After the converter reached the \(D^3\), the current was measured and converted into STH efficiency, as derived from eq 4. The measured current densities per light-irradiated area (converted STH efficiency from measured current on EC) were 16.81 mA cm\(^{-2}\) (20.6%), 15.96 mA cm\(^{-2}\) (19.6%), and 15.56 mA cm\(^{-2}\) (19.1%) when \(A_{\text{EC}}/A_{\text{PV}}\) was 3, 1.5, and 1, respectively. STH efficiencies were lower than the value driven from Figure 3b. The lower efficiency can be related to the converter efficiency because the converter actually used a small amount of PV power for its operation. Without the converter application, 18.4% STH efficiency can be measured (Figure S9).

For an in-depth understanding of (vii) \(\eta_{\text{conv}}\) and the discrepancy between \(D^3\) and \(D^3\), we analyzed the converter efficiency with \(D^3\) condition at the given \(A_{\text{EC}}/A_{\text{PV}}\) configuration. At each \(D^3\), \(\eta_{\text{conv}}\) can be calculated by dividing the electrical power consumed on the EC by photogenerated PV power as follows

\[
\eta_{\text{conv}} = \frac{I_{\text{EC}} \times V_{\text{EC}}}{I_{\text{PV}} \times V_{\text{PV}}} 
\]

Because all used \(I_{\text{EC}}, V_{\text{EC}}\) at the EC and \(I_{\text{PV}}\) and \(V_{\text{PV}}\) at the PV can be measured by a potentiostat and voltmeter, \(\eta_{\text{conv}}\) at each configuration can be derived (Figure 3d). Interestingly, \(\eta_{\text{conv}}\)
increased when higher $A_{EC}/A_{PV}$ EC configuration was used. For instance, approximately 95.9% $\eta_{conv}$ can be achieved when $A_{EC}/A_{PV}$ was 3, which is far higher than 92.8% $\eta_{conv}$ when $A_{EC}/A_{PV}$ was 1.

Note that the degree of consistency between $D^0$ and $D^T$ ($D^T/D^0$) in Figure 3b becomes larger with higher $A_{EC}/A_{PV}$ EC configuration. Moreover, the values between $\eta_{conv}$ and $D^T/D^0$ are almost identical, indicating a correlation between the two parameters. The correlation can be theoretically derived from the following equation

$$\eta_{conv} = \frac{I_{PV}}{I_{EC}} \times \frac{V_{EC}}{V_{PV}} \times \frac{V_{PV}}{V_{PV}} = \frac{[V_{EC}/V_{PV}]/[I_{PV}/I_{EC}]}{D^0} = D^T/D^0$$

(6)

The transformation of the $I_{PV}/I_{EC}$ value into $D^0$ is based on our observation of equivalency with two values (Table S1). The consistency between $I_{PV}/I_{EC}$ and $D^0$ can be attributed to the relatively large inductance (1 mH) of our converter with an operation frequency of 20 kHz, which significantly reduces the ripple current of the inductor in the converter. Additionally, because $V_{EC}/V_{PV}$ during the MPPT process was identical to $D^T$, $\eta_{conv}$ and $D^T/D^0$ values agreement can also be derived (Figure 3d). Despite controlling the input duty ($D$) as not to be identical to $D^0$ at each configuration, equivalence between $\eta_{conv}$ and ($V_{EC}/V_{PV}$) ($1/D$) was still maintained, indicating the validity of eq 6.

We also acknowledged that $\eta_{conv}$ becomes lower as $D^0$ becomes higher. The high $D^0$ value is identical to the technical situation where switch $S_1$ in Figure 3a is mostly in the turn-on position. Hence, this indicates that a longer time in the turn-on position can severely reduce the conversion efficiency of our system. To prove that $\eta_{conv}$ is dependent on the input duty ratio and not on the amount of PV-generated electrical power, we investigated $\eta_{conv}$ in terms of deliberately controlled input duty ratio ($D$) at a fixed $A_{EC}/A_{PV}$ (=1) configuration and found that $\eta_{conv}$ increased with lower $D$ (Figure 3e). This further strengthens our claim that a small duty can actually increase the converter efficiency. The $\eta_{conv}$ in terms of $D$ at a fixed $A_{EC}/A_{PV}$ configuration followed a similar trend as the $\eta_{conv}$ in terms of $D^0$ in Figure 3d, indicating that rather than the amount of PV-generated power, the duty ratio value plays a huge role in the $\eta_{conv}$ of our system. Therefore, we can hypothesize that as the number of series-connected PV increases, lower optimized duty will be necessary for the MPPT process and also for the generation of high-converter efficiency.

To further understand the converter efficiency and its operation with various duties, we observed the operation of the PV-Conv-EC system by varying (vii) the number of series-connected PVs. The $D^0$ for MPPT was completely different from two series-connected PV systems. For instance, by series-connecting three GaAs PVs, much lower $D^0$ is required compared with a two-series-connected PV configuration (Table 1). Interestingly, under PVs with three series-connected configurations, dramatic improvement in the STH efficiency (19.5%) can be achieved when $A_{EC}/A_{PV} = 1$, compared with 12.2% STH efficiency without the converter application (Figure S10c). The $\eta_{conv}$ of three series-connected PVs that used the PV-Conv-EC system was higher than that of the two series-connected PV system because of the lower $D^0$ required for the MPPT process at $A_{EC}/A_{PV} = 1$ configuration. Therefore, the number of series-connected PVs plays a significant role in determining the $\eta_{conv}$ of the converter MPPT process. Moreover, by using boost-type converter, the system allows MPPT of non-series-connected PVs to operate water electrolysis, although $V_{DC}$ is much lower than 1.23 V as shown in Table 1. Despite the low $\eta_{conv}$ with non-series-connected PV, hydrogen can be generated where conventional PV-EC system is not available (Figure S10d).

In an identical PV and EC area, the PV-Conv-EC system can also be used to various (ix) solar light power densities. By measuring the $I$–$V$ curve of the PV at various light densities, the current and $D^T$ based on the $V_{EC,MPPT}/V_{PV,max}$ ratio can be predicted as shown in Figure 4a. When the solar power densities are 70 and 30 mW cm$^{-2}$, the estimated current of the EC at each light density divided solar cell area will be 11.97 (20.9% STH) and 5.09 mA cm$^{-2}$ (20.8% STH). Similar to that shown in Figure 3b, relatively lower power generated from the PV would guarantee higher STH and lower $D^T$ for MPPT (Figure 4a). By measuring the $I_{EC}$ generated from different light irradiance powers, the STH efficiency can be performed and the duty can be optimized (Figure 4b). Interestingly, we found that MPPT can occur at each light irradiance power for achieving the highest STH efficiency by the use of $P_{PV,max}$. Therefore, our system can always use the maximum power of the PV at any time even though it changes because of the light intensity. The STH efficiency at a small light irradiance power was provided at both high STH and converter efficiency. Current densities of 11.29 mA cm$^{-2}$ (19.8% STH) and 4.92 mA cm$^{-2}$ (20.1% STH) can be achieved, respectively, at 70 and 30 mW cm$^{-2}$ of light irradiance to PVs. The stability of our system was also confirmed under the 30 mW cm$^{-2}$ light condition (Figure 4c). These show the possibility that our system can truly achieve the maximum STH even with the varying intensity of solar light through the combination of an automatic perturbation and observation (P&O) algorithm. Moreover, if we can obtain spectra on each solar light intensity, it would be possible to firmly analyze the relationship between the STH efficiency and solar light intensity based on light absorption and conversion prediction of our GaAs PVs as the Deutsch group suggested and the modeling we did on Figure 1.34 It will further improve the robustness of our design principle so that our system has more industrial applications.

### CONCLUSIONS

The advantage of this approach is that the decoupled factors in terms of PV and EC variables can be investigated to determine how they can affect the final efficiency of a PV–EC system. Our findings provide new insights into the selection of independent PV and EC compartments for achieving the desired efficiency
achieved. Even if the rare metal electrocatalysts were used for 4000 s at 30 mW cm$^{-2}$ and solar power density. (c) Current density measured at the EC for STH and $D_{\text{cat}}$. The STH efficiencies under each condition are converted from each current efficiency outlined in Figure S1. We assume that the temperature was maintained at room temperature in the modeled solar cell or PV-Conv-EC system.

**Fabrication of the Solar Cell.** The GaAs solar cell was fabricated by the following process. First, the device layer was deposited on the GaAs wafer by metalorganic chemical vapor deposition (MOCVD) in the following order: trimethylgallium (TMGa), arsine (AsH$_3$), trimethylaluminum (TMAl), phosphine (PH$_3$), and trimethylindium (TMIn). Next, by using the e-beam evaporator, the front and back of the gold electrode were deposited. The front layer was additionally electroplated for decreasing the resistance with the optimized grid structure. To control the surface area, the mesa-etching process was conducted. To be specific, the cell with a designated area (1 cm$^2$ in this case) was covered with a photoresist and etched with solution. After the etching is completed, the photoresist was peeled off. After cutting the cell into the desired form, the cell was bonded on a printed circuit board (PCB) substrate, and the front electrode was wired with the substrate. Finally, for the antireflective coating, the ZnS and MgF$_2$ layers were thermally evaporated and deposited on the solar cell with optimized thickness (~50 and ~100 nm for ZnS and MgF$_2$, respectively).

**Synthesis of Electrode.** The metal oxide nanocrystalline was synthesized using the hot injection method. After washing the nanocrystalline with toluene and acetone, 20 mg of the synthesized nanocrystalline was annealed under 250 °C for 1 h for removing organic ligands. The annealed nanocrystalline was dispersed in 50 mL of 1 mg ml$^{-1}$ K$_2$IrCl$_6$ (STREM, 99%) and heated at 60 °C for 6 h under continuous stirring. The powder was washed with water and ethanol. After washing, annealing was conducted under 250 °C for 1 h. After the annealing procedure, 1.2 mg of IrO$_2$ powder was dispersed in 120 μL of ethanol and 9 μL of Nafion 117 solution (Alidar, ~5 wt % mixture of alcohol and water). A drop of ink was placed on 6 cm$^2$ carbon fiber paper (FuelCellStore, Spectracarb 2050A-0850) and dried under ambient condition for 1 day. The cathode was prepared with 1.2 mg of 20 wt % Pt/C (Alfa) and dispersed in 120 μL of ethanol and 9 μL of Nafion 117 of a solar-driven hydrogen evolution reaction. The individual compartment-dependency and the interface optimization presented here highlight the selection of an EC catalyst and the optimized configuration that derives the highly efficient photoelectrolysis hydrogen evolution, minimizing the loss. Through the optimization modeling and experiments, the importance of EC performance especially with highly efficient PVs, converter existence, and optimized number of series-connected PVs are indispensable for a high STH-efficiency PV-Conv-EC system. As a result, 20.6% STH efficiency and 78% PV electricity-to-hydrogen conversion efficiency can be achieved. Even if the rare metal electrocatalysts were used for this work, we definitely believe that state-of-the-art earth-abundant catalysts can be also used to our design principle because of their superior characteristics. 27 This PV-Conv-EC system design rule can help advance the commercialization of solar-driven hydrogen fuels for a future clean-energy society.

**METHODS**

**Model Study.** From the analysis of Figure 1c, the fixed parameters of eqs 2 and 3 were calculated as follows: $t_{\text{cat}} = 30$ mV dec$^{-1}$, $t_{\text{ano}} = 60$ mV dec$^{-1}$, $I_{\text{cat}} = 1$ mA, and $R_{\text{col}} = 1$ Ω cm$^2$. The $R_{\text{cat}}$, $R_{\text{ano}}$, and $\eta_{\text{10mA}}$ values correspond to the Tafel mechanism of hydrogen evolution, the one-proton-one-electron-involved water oxidation mechanism, and the exchange current of platinum for hydrogen evolution, respectively.35,36 In Figure 1d, the variation in the $t_{\text{cat}} + t_{\text{ano}}$ and $\eta_{\text{10mA}}$ values were brought about by the anode performance under a fixed cathode performance condition (cathode exchange current = 1 mA and Tafel slope = 30 mV dec$^{-1}$). The PV used in this figure was with 30% efficiency, as shown in Figure S1. The resistance was also fixed, $R_{\text{col}} = 1$ Ω cm$^2$, as in Figure 1c,d. In Figure S2, the anode performance was fixed as the anode exchange current density = $10^{-3}$ mA cm$^{-2}$ and the Tafel slope = 60 mV dec$^{-1}$. The cathode performance was fixed as cathode exchange current = 1 mA cm$^{-2}$ and the Tafel slope = 30 mV dec$^{-1}$. The PV used in this figure was with 30% efficiency, similar to the efficiency outlined in Figure S1. We assume that the temperature was maintained at room temperature in the modeled solar cell or PV-Conv-EC system.

**Fabrication of the Solar Cell.** The GaAs solar cell was fabricated by the following process. First, the device layer was deposited on the GaAs wafer by metalorganic chemical vapor deposition (MOCVD) in the following order: trimethylgallium (TMGa), arsine (AsH$_3$), trimethylaluminum (TMAl), phosphine (PH$_3$), and trimethylindium (TMIn). Next, by using the e-beam evaporator, the front and back of the gold electrode were deposited. The front layer was additionally electroplated for decreasing the resistance with the optimized grid structure. To control the surface area, the mesa-etching process was conducted. To be specific, the cell with a designated area (1 cm$^2$ in this case) was covered with a photoresist and etched with solution. After the etching is completed, the photoresist was peeled off. After cutting the cell into the desired form, the cell was bonded on a printed circuit board (PCB) substrate, and the front electrode was wired with the substrate. Finally, for the antireflective coating, the ZnS and MgF$_2$ layers were thermally evaporated and deposited on the solar cell with optimized thickness (~50 and ~100 nm for ZnS and MgF$_2$, respectively).

**Synthesis of Electrode.** The metal oxide nanocrystalline was synthesized using the hot injection method. After washing the nanocrystalline with toluene and acetone, 20 mg of the synthesized nanocrystalline was annealed under 250 °C for 1 h for removing organic ligands. The annealed nanocrystalline was dispersed in 50 mL of 1 mg ml$^{-1}$ K$_2$IrCl$_6$ (STREM, 99%) and heated at 60 °C for 6 h under continuous stirring. The powder was washed with water and ethanol. After washing, annealing was conducted under 250 °C for 1 h. After the annealing procedure, 1.2 mg of IrO$_2$ powder was dispersed in 120 μL of ethanol and 9 μL of Nafion 117 solution (Alidar, ~5 wt % mixture of alcohol and water). A drop of ink was placed on 6 cm$^2$ carbon fiber paper (FuelCellStore, Spectracarb 2050A-0850) and dried under ambient condition for 1 day. The cathode was prepared with 1.2 mg of 20 wt % Pt/C (Alfa) and dispersed in 120 μL of ethanol and 9 μL of Nafion 117
solution. A drop of ink was placed on 6 cm² carbon fiber paper and dried under ambient air for 1 day.

**Converter Designing.** To implement the converter, the FR-4 PCB was designed on the breadboard with appropriate devices. The switches of the converter (S₁ and S₂) were both implemented by MOSFET (IRF 540). The 1 mH ferrite core inductor, SRR 1208-102KL, was used as the inductor. The appropriate duty cycle control was exercised with the digital signal processor TMS320C28346 from Texas Instruments. The switching frequency was 20 kHz.

**Material Characterization.** The IrOₓ nanocrystalline was analyzed using a transmission electron microscope (JEOL, JEM-2100F). The Pt/C nanocrystalline was measured using a field-emission scanning electron microscope (Carl Zeiss, SIGMA).

**MEA Cell Construction.** The configuration of the cell is shown in Scheme 1. The Nafion membrane was washed under boiling 3 wt % H₂O₂ for 1 h, boiling 1 mol L⁻¹ H₂SO₄ for 1 h, and boiling deionized water for 1 h before each assembly. The interface between the graphite bipolar plate and the Nafion membrane was joined with a silicon (~0.2 mm) gasket with both the cathode and anode sites. The cell was sealed with torque of a 75 kgf cm at each screw driver. The carbon fiber paper electrode area was fixed at 6 cm² for each cathode and anode.

**Electrochemistry.** Electrochemical measurements were recorded using a potentiostat (CHI 760E, CH Instruments). For three electrochemical measurements, a Pt foil (3 cm x 3 cm, 99.997% purity, Alfa) was used as the counter electrode, and Ag/AgCl electrode (BASi, 3 M NaCl) was used as a reference electrode. In the case of 3 electrode system, 0.5 cm² of catalyst electrode performance was measured. The working electrode was prepared by following the procedure similar to the previous drop-cast carbon fiber paper. The scan rate was 10 mV/s. The catalyst property was shown after polarization between the forward and reverse CV scan current and further iR compensation using $V = V_{appplied} - iR$.

The electrochemical potentials were converted into the RHE scale by the following equation

$$E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 + 0.0592 \times \text{pH}$$

For the two-electrode electrochemical measurements, the counter and reference electrodes were connected to the cathode compartment of the MEA cell and the working electrode was connected to the anode compartment. The electrolyte was prepared with 0.1 mol L⁻¹ HClO₄ for both the three and two electrochemical measurements. The current detection during the photovoltaic-based electrolysis was measured by the same potentiostat connected to the ammeter. The voltage during photocell was measured based on the converter voltage measurement.

**Gas Measurement.** Gas quantification was performed using gas chromatography (GC). The hydrogen evolution compartment of the MEA cell was connected and hermetically sealed in a glass flask. Before electrolysis, Ar gas was purged for 15 min to eliminate the gas content. After sealing of the gas, bulk electrolysis was started under 1.6 V until a charge was accumulated. For each given charge, 1 mL of gas was collected using a gas-tight syringe and injected into a gas chromatography instrument (NARL8502 model 4003, PerkinElmer). The oxygen evolution was analyzed using a fluorescence-based oxygen probe (NEOFOX-KIT-PROBE, Ocean Optics). A similar procedure for the detection of H₂ evolution was performed: the MEA cell anode compartment was tightly linked with a glass flask containing an electrolyte. After purging with Ar for 15 min, bulk electrolysis was conducted under 1.6 V while the oxygen probe detected the oxygen in the glass flask.

**Solar Cell IV Curve Measurement.** For a single GaAs PV, the current–voltage performance was measured by applying external potential by an $I$–$V$ test system (K3000, MsScience). The solar simulator (K3000, MsScience, class AAA) was used to irradiate the standard light condition on the GaAs PV and PV-conversion system under the AM 1.5 G (100 mW cm⁻²) condition or a specific solar power density condition. During the PV performance measurement or PV-conversion system operation, the PVs are always cooled with a fan for maintaining consistent room temperature. The PV area was controlled by a combination of 1 cm² of monolithic GaAs PV. The light intensity variation was measured using an optical power meter (Newport, model 1916-R).

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00012.

$I$–$V$ curve of modeled PVs in Figure 1c and their performance; $P_{EC}$ of the PV-Conv-EC at a given EC electrode area to the light-illuminated PV area ratio ($A_{EC}/A_{PV}$) and electrolyte resistance at 30% PV efficiency and fixed EC performance; three-electrode-based current density–voltage ($j$–$V$) curve of IrOₓ anode and Pt/C cathode used on the MEA cell at 0.1 mol L⁻¹ of HClO₄ (pH 1) solution; the resistance of the EC compartment when 1.6 V was applied to the EC compartment; time-dependent H₂ evolution of the MEA cell; oxygen evolution reaction of the EC at 1.6 V with the IrOₓ anode; $j$–$V$ curve and performance of PV with different surface areas and light-irradiation powers; photograph of the PV-Conv-EC system; current density and STH efficiency under chopped illumination on the PV-Conv-EC system and the PV–EC system without a converter; STH prediction and measured value of the PV-Conv-EC system with different PV connection configurations; measured PV-to-EC current ratio, voltage ratio, and converter efficiency at different input duties with various $A_{EC}$-to-$A_{PV}$ ratios as shown in Figure 3d.

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**Notes**

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