Integrated Photo-Electrochemical Solar Fuel Generators under Concentrated Irradiation

II. Thermal Management a Crucial Design Consideration

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The solar energy received on earth’s surface, capable of meeting mankind’s current and future energy demands,1-4 can be directly converted into electricity using photovoltaic cells. However, electricity is difficult and costly to store, and considerable losses are accrued when attempting to distribute it over long distances. This problem can be circumvented by directly converting the photon energy into fuels. The simplest reaction considered is the electrolysis of water to produce hydrogen. Hydrogen can become a complementing energy fuel in addition to other strategies.6 Hydrogen can also serve as a carrier and can be used as an energy-rich reagent for the exothermic formation of methane, methanol, or hydrocarbons using atmospheric CO₂ as a carbon feedstock. To realize this goal, practical means for formation of methane, methanol, or hydrocarbons using atmospheric CO₂ are needed. Today more than 95% of global hydrogen production is based on steam reforming of fossil fuels.6 A promising sustainable approach to hydrogen production is solar driven, using integrated photo-electrochemical (PEC) pathways. An IPEC device is defined as a device in which an area-matched photoabsorber and electrocatalyst are in direct contact. We propose an integrated photo-electrochemical device design, shown in Fig. 1. This device profits from the exclusion of direct semiconductor-electrolyte interfaces prone to interface degradation issues, and limits the transmission losses occurring in completely un-integrated, externally wired photovoltaic plus electrolyzer systems. The design incorporates an electronic conductor for the transfer of charge carriers from the photoabsorber to the reaction site – as contrasted with devices designed with an ionic conductor – in order to reduce the overpotentials and to benefit from larger conductivities.6 A key issue for the economic competitiveness of PEC devices is the reduced use of rare and expensive device components, such as catalysts and light absorbers,7 which is addressed through concentrating the solar irradiation. Two examples of experimental investigation of non-integrated PEC devices using concentrating irradiation demonstrate that very interesting efficiencies can be achieved.8,9 However, irradiation concentration leads to driving current densities which are approximately proportional to the concentration factor, thus inducing larger overpotentials and possible mass transport limitations.10 Optical concentration generally increases the device temperature and consequently enhances the kinetics and the ionic transport in the solid electrolyte (its conductivity drops, however, at temperatures above 120 °C due to membrane dry out11,12) while reducing the performance of the photoabsorbers.13 A (concentrated) integrated photo-electrochemical device allows heat transfer between the components: transferring heat from components whose performance suffers from high temperature operation to components whose performance benefits from high temperature operation. Therefore, the overall performance of concentrated integrated photo-electrochemical (CIPEC) devices can potentially gain from the reduced use of direct semiconductor-electrolyte interfaces. This benefit can be provided by concentrating solar irradiation for use in integrated photo-electrochemical devices.10

Concentrating solar irradiation for use in integrated photo-electrochemical devices potentially provides an economically competitive pathway for hydrogen generation, even with partial use of rare material components. Heat transfer and thermal management are crucial in devices operating under large irradiation concentrations. With dedicated thermal management, detailed 2-dimensional multiphysics modeling predicts high performance. Two competing operational parameter spaces are observed: (i) thermal effects enhance performance in the zone of low operational current density, and (ii) mass transport limits dominate in the zone of high operational current density (saturation current of the electrolyzer component). These competing effects lead to tradeoffs between device efficiency and hydrogen evolution rate, quantified using Pareto frontiers. Smart thermal management – only possible through integrated device design – helps in achieving efficient and low cost production of solar fuels, and can further alleviate degradation-related performance decreases over the lifetime of the device. For example, at an irradiation concentration of 707, a 12% degradation in STH efficiency of a Si-based device is compensated by a seven-fold increase in the water mass flow rate. Integrated photo-electrochemical device designs combined with smart thermal management prove to be a practical and economically feasible approach to solar fuel processing, and provide a pathway to circumvent limitations imposed by materials.7

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Figure 1. Schematic (not to scale) showing (a) the top view and (b) the side view of the integrated PEC device depicting incoming concentrated irradiation, cooling and preheating water channel, triple/dual-junction PV, and the integrated electrochemical system consisting of anodic and cathodic channels, gas diffusion layers (GDL), catalyst layers, and a polymeric electrolyte (Nafion). The 2D simulation domain is the plane shown in (a). A 3D schematic is shown in Tembhurne et al. The water from the top water channel is fed to the anodic chamber shown in (a) with green arrows. The PV’s top p-type contact is connected to the titanium port and reacting fluid flow, and heat transfer (HT) is presented in our companion paper.

The water at the outlet of the water channel is fed to the anodic chamber at its inlet with normal velocity, \( \nu_{\text{mean}} \). The heat source in the electrochemical system is comprised of electro ohmic losses, electrolyte ohmic losses and kinetic losses, is given by:

\[
Q_{\text{EC}} = -J \cdot \nabla \phi_a - J \cdot \nabla \phi_f + \left( \phi_a - \phi_f - E_{\text{eq}} + T \frac{\partial E_{\text{eq}}}{\partial T} \right) i_{\text{loc}}.
\]

For heat transfer, the steady-state energy conservation equation is solved using finite element methods and a MUMPS solver. The fluid flow and mass transport in the channels and the porous gas diffusion layers (GDLs) are modelled by the Navier-Stokes equation with inlet velocity and normal velocity, \( \nu_{\text{mean}} \).

Charge transport in the semiconductor (SC), the Poisson equation and current conservation equations are solved simultaneously using Fermi-Dirac statistics and a finite volume solver, incorporating the transport of electrons via the electron current density vector, \( J_e \), and holes via the hole current density vector, \( J_h \), where their sum gives the total current density. The internal heat source term in the semiconductor is given by

\[
Q_{\text{PV}} = J \cdot \nabla V + (E_g + 3k_B T) R.
\]

where \( R \) is the net recombination. The first term \( J \cdot \nabla V \) represents the ohmic losses, and the second term \( (E_g + 3k_B T) R \) gives the recombination losses in the semiconductor. A detailed modeling methodology for the semiconductor simulation, electrochemical (EC) charge transport and reacting fluid flow, and heat transfer (HT) is presented in our companion paper.

Charge transport in the electrolyte is simulated by the current conservation and Nernst-Planck equations, obeying electro-neutrality. Ohm’s law is used for the current conservation in the electrode. The electrochemical reaction at the electrode-electrolyte interface is accounted for via the reaction current, \( i_{\text{vol}} \), modeled via the Butler-Volmer expression for the anodic one-step oxygen evolution reaction (OER),

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^-.
\]

and cathodic one-step hydrogen evolution reaction (HER),

\[
4H^+ + 4e^- \rightarrow 2H_2.
\]

The charge conservation equations in the electrode and electrolyte are solved via finite element methods and a MUMPS solver. The fluid flow and mass transport in the channels and the porous gas diffusion layers (GDLs) are modelled by the Navier-Stokes equation with Darcy extension. Species transport for the low density fluid mixture is modelled by the Maxwell-Stefan diffusion model. The water at the outlet of the water channel is fed to the anodic chamber at its inlet with normal velocity, \( \nu_{\text{mean}}\). The heat source in the electrochemical system is comprised of electro ohmic losses, electrolyte ohmic losses and kinetic losses, is given by:

\[
Q_{\text{EC}} = -J \cdot \nabla \phi_a - J \cdot \nabla \phi_f + \left( \phi_a - \phi_f - E_{\text{eq}} + T \frac{\partial E_{\text{eq}}}{\partial T} \right) i_{\text{loc}}.
\]

Results and Discussion

Two reference cases were defined, utilizing i) a triple junction thin film aSi-ucSi-ucSi cell having a p-n-cathodic-anodic configuration, and ii) a dual junction III-V based Ga0.51In0.49P-GaAs cell incorporating a n-p-anodic-cathodic configuration. Henceforth, reference case I refers to the thin film Si based, and case II refers to the III-V based integrated PEC device. The input to the PV is assumed to come from a perfect concentrator with 100% optical efficiency and an AM1.5G
The slope of the linear region of the EC curves decreases with decreasing mass flow rate, see Fig. 2, due to increased charge transport losses, mostly resulting from the increased temperature of the stream. The saturation current of the EC decreases with decreasing mass flow rate due to mass transport limitations occurring in the porous electrodes. Due to this behavior, the EC curves for varying mass flow rates at a given concentration intersect in a small voltage range, giving rise to two regions of characteristic operation for the device (indicated as regions I and II). In region I, at a particular C, the EC curves shift to the right side on the voltage scale with increasing mass flow rate, while in the region II they shift to the left side. The identification of the two characteristic operating regions explains the performance effects observed for varying concentrations: increasing the concentration from small to large values shifts the operational point from region I to region II, resulting in the previously discussed trend for H₂ production rates and STH efficiencies. The stronger changes observed for concentrations above 450 result from operation in the falling region of the J-V curve of the PV, leading to a drastic efficiency decrease with mass flow rate decrease.

Average EC and PV temperatures, Figs. 3c–3d, decrease with increasing water mass flow rates. At a mean flow velocity of 0.03 m/s, there is a 40-fold increase in the $Q_{EC}$ (EC heat source) when going from C = 53 to 1000. At a mean flow velocity of 2 m/s, for the same concentration range, the increase in the $Q_{EC}$ is 48-fold. Similar behavior is observed for the PV heat source, $Q_{PV}$. However, despite of significant increases in heat sources, the temperature increase in the EC and PV at large mass flow rates is only a few Kelvins, as opposed to increases in temperature of tens of Kelvins for low mass flow rates. These results imply that higher water mass flow rates have a better cooling capability than low mass flow rates. Additionally, high mass flow rates allow the operation at high C with increased saturation of EC, and hence increased operating currents.

The optimum region of device operation for highest H₂ production occurs in the large concentration range (700-1000) at large water mean flow velocities (0.1-2 m/s). In contrast, the preferred region of operation maximizing the STH efficiency lies in the low concentration range and is independent of the mean flow velocities in the inspected range (0.03-2 m/s). This competitiveness in the
Figure 3. Contour plots showing the evolution of (a) hydrogen production rate [g/min/m²], (b) STH efficiency, (c) average PV temperature [K], and (d) average EC temperature [K], as a function of varying irradiation concentrations and water mean flow velocities for reference case I. (e) Operating STH efficiency for varying mean flow velocities and $C$ as a function of hydrogen production rate. The Pareto front in (e) is shown by the dotted black line. The color of the circles represents concentration and the color of the stars represents the mean flow velocity [m/s].

objectives of H₂ production and STH efficiency is plotted in Fig. 3e. With the aim of having increased H₂ production along with increased STH efficiency, we observe that the various operating conditions form a Pareto front implying the absence of a global optimum but the existence of a range of semi-optimal efficiencies and hydrogen production rates. The frontier has no specific trend with respect to $C$, but consists mainly of parameter combinations with the highest mean flow velocity. The optimum mean flow velocity is around 0.2 m/s, as evident from Fig. 3, above which the variations in STH efficiency, H₂ production, and temperature become negligibly small.

For reference case II, i.e. with a dual junction Ga₀.₅₁In₀.₄₉P-GaAs, the characteristic curves and variations of the objective functions are presented in Figs. S.1 – S.2. A similar behavior as for the reference case I is observed, including the formation of the two distinct operational regions (I and II). However, the bandgaps for the Ga₀.₅₁In₀.₄₉P-GaAs cell are more sensitive to the temperature, and therefore a clear difference in the PV J-V curves with changing mass flow rates is observed. The optimal concentration is at $C = 180$ and a mean flow velocity of 0.2 m/s. For larger concentrations the $J_{sc}$ of the PV is always larger than the saturation current of the EC (i.e. for the case when PV area is equal to EC area as shown in Fig. 1). The $J_{op}$, and therefore $M_{H₂}$, minimally increase with increasing mean flow velocity until $C = 150$, and significantly increase for $C = 150$ to 1000. The STH efficiency increases with increasing mass flow rate. For reference case II, the $J_{op}$ and STH efficiency trends are not the same as for the reference case I. There is no reversal in trend for H₂ production and STH efficiency as C increases, despite the formation of two distinct operational regions. This follows from the location of the operational points, which always lie in region II. The temperature variations show the same behavior as reference case I. The tradeoff between H₂ production and STH efficiency also leads to a Pareto front for reference case II. However, this front is relatively flat and closer to a global optimum. For reference case II, ~100% of the maximum STH efficiency and ~96% of the maximum H₂ production can be chosen at the same time whereas for reference case I the best configuration turns out to be the one with 50% of the maximum of both objective functions.

The regions of enhanced performance for the thin film Si based device and III-V based device are quantified in Figs. 4a and 4b respectively. The contour plot of Fig. 4a agrees with the STH efficiency trend reversal after $C = 300$ shown in Fig. 3b. The $x$-axis value of 1 corresponds to the reference mean flow velocity, $v_{\text{mean}}^{0}$, of 0.2 m/s. $\eta_{\text{STH}}^{0}$ is the STH efficiency at 0.2 m/s for the corresponding concentration. Fig. 4a shows that maximum efficiency enhancement is observed for $C > 300$ and 0.1 m/s $\geq v_{\text{mean}} \geq 0.03$ m/s. For example at
C = 546, the STH efficiency increases by 9.2% when \( v_{\text{mean}} \) increases from 0.03 to 0.2 m/s. For the III-V based case, the significant STH efficiency improvement is seen for \( C > 180 \) and 0.1 m/s \( \geq v_{\text{mean}} \geq 0.03 \) m/s. For example at \( C = 546 \), an efficiency increase of 17.5% is observed for an increase in \( v_{\text{mean}} \) from 0.03 to 0.2 m/s. Both plots show that there are large efficiency enhancements for higher concentrations with increases in the mass flow rates.

In summary, the mass flow rate plays an integral role in thermal management in integrated devices. IPEC devices can be operated without significant decrease in performance, even at very high irradiation concentrations, provided the water flow velocity in the cooling channel is at least 0.2 m/s. The changing mass flow rate doesn’t affect the performance at low \( C \), but has the potential to significantly improve STH efficiency for larger concentrations. When operating in region II (often given at high \( C \)), the mass flow rate allows for control of the operating point of the integrated device and thus can be used as a controlling parameter to counteract component degradation over the device lifetime. This is particularly pronounced if operation is close to the maximum power point of the PV. We predict that the device degradation and the corresponding decrease in performance over the lifetime of the system can be controlled by smart thermal management. For operation of the Si-based device at \( C = 707 \), a 12% degradation in STH efficiency can be compensated with a seven-fold increase in the water mass flow rate if the operating point remains in region II, i.e. degradation overpotential in the EC is limited to about 250 mV. This shows that smart thermal management - possible due to the integrated nature of our device design - contributes significantly to a device with stabilized and high performance over an elongated fraction of device lifetime. Additionally, thermal management controls and/or reduces the component temperature, which is expected to further reduce the rate of thermally-induced degradation phenomena.

**Material choices.**—Catalyst characteristics.—The catalysts characteristics investigated are exchange current density and active specific surface area (ASSA). For reference case I, the exchange current density for each electrode and its temperature variation is given in Table S.1, representing Pt and IrO2 catalysts. The evolution of produced H2 and STH efficiency of the device for varying exchange current densities of the anodic and cathodic reactions is shown in Figs. 5a–5b. \( M_{\text{IrO2}} \) increases with increasing exchange current densities at a given concentration. This increase is only significant in a concentration range between 250 and 650. Outside this range \( J_{\text{IrO2}} \) varies minimally. This behavior results from the location of the operational points, which lie either in the flat region of the PV (for \( C < 250 \)) or in the saturation region of the EC (for \( C > 650 \)). A similar trend is observed for the STH efficiency resulting from the nature of the J-V curves, Fig. S.3. The EC’s J-V curves start separating as the voltage increases above \( E_{\text{eq}} \) due to the increased activation overpotential at smaller exchange current densities. The EC’s J-V curves stay almost constant (parallel) in the linear region, as ohmic losses are not affected, and coincide toward the saturation region. This behavior implies that the mass transport limit is not affected by the change in exchange current density.

The active specific surface area (ASSA) is defined as active surface area divided by the volume. The variation of \( M_{\text{Pt}} \) and STH efficiency with \( C \) and ASSA show very similar behavior to the varying exchange current density multiplier case. Hydrogen production was found to minimally increase with increasing ASSA for \( C \leq 600 \). For larger \( C \), \( J_{\text{Pt}} \) becomes independent of ASSA. The STH efficiency increases significantly at medium \( C \) (∼9.8% increase for increase in ASSA from \( 10^{3} \) to \( 10^{6} \) m\(^{-1}\)) at \( C = 450 \), but remains constant at large \( C \). The J-V curves of the EC show similar trends to those observed for changing exchange current densities.

Maximum H2 production can be achieved at a large concentration (\( C = 700–1000 \)) independent of the chosen exchange current density and ASSA. However, maximal STH efficiency is achieved at the lowest \( C \) and highest exchange current density, utilizing electrodes with large ASSA. This contradictory choice for optimized operation results in a Pareto front, Figs. 5c–5d. The fronts are comprised of devices which utilize the largest exchange current densities or ASSA.

In summary, at large irradiation concentration, the exchange current density and ASSA do not affect the operating current density, and consequently we predict a production rate insensitive to the chosen catalysts. However, the efficiency increases (by 7.8% for exchange current density increase by factor of 100) for the case with \( C = 546 \) when the catalysis is enhanced. The highest exchange current density and the ASSA are required for device operation on the Pareto front, i.e. compromising between efficiency and hydrogen production. A ∼9.5% increase in hydrogen production caused by increasing the multiplier from 1 to 100 at \( C = 450 \) only causes a ∼0.3% increase in temperature. Similar behavior is observed for temperature variations for the ASSA analysis. This insensitivity of the temperature, despite a significant increase in the heat source, is a result of smart thermal management, with a mean flow velocity of 0.2 m/s, which is the optimized value, see Operating conditions: Irradiation concentration and water mass flow rate section.

**Dimensions and design.**—Membrane thickness.—The variation of thickness of the solid electrolyte (a Nafion membrane) affects the diffusion driving force of the ions across the membrane and the membrane’s concentration-dependent conductivity. The J-V curves for varying membrane thickness (30-100 um), Fig. 5.4, show that the operating point changes significantly with changing membrane thickness. Changing membrane thickness has a large impact on the device performance for large \( C \) because, in this case, the operating points lie in the falling region of the PV’s J-V curve. The concentration overpotential and ohmic losses are significantly affected by membrane.
thickness. They increase with increasing thickness with no change in the activation overpotential.

The variation of the amount of H2 produced with varying membrane thicknesses and for different irradiation concentrations is shown in Fig. 6a. $J_{\text{op}}$, and hence H2 production, decrease insignificantly with increasing membrane thickness up to $C = 200$. For $C > 200$, the decrease in $J_{\text{op}}$ becomes drastic, i.e. $\sim 60\%$ decrease at $C = 546$. A similar behavior is observed for the STH efficiency, Fig. 6b. Maximum H2 production occurs at the largest $C$ and for the thinnest membrane, while the STH efficiency is maximal for small $C$ and independent
of the membrane thickness. The tradeoff between H₂ production and STH efficiency is shown in Fig. 6c, showing a Pareto frontier. The Pareto front includes the smaller membrane thickness, but no specific trend exists for C.

The average PV and EC temperatures, Fig. S.4(e)-(f), show minimal variations at a given C with varying membrane thickness. However, for an example case with C = 1000, QEC increases by 2.7 times and Qpv by 1.21 times as the membrane thickness decreases from 100 to 30 μm. This increase in the overall heat source at a large irradiation concentration is a direct result of the large variations in the operating current. This behavior is also observed for C > 200. The temperature variation is only a few Kelvins for this heat source increase, indicating that the device has a good thermal management, which is the result of the water flow velocity choice of 0.2 m/s, an optimized velocity according to mass flow rate analysis (see Operating conditions: Irradiation concentration and water mass flow rate section). The average PV temperature remains constant for low irradiation concentrations. At large C for increasing membrane thicknesses, the PV temperature decreases and this rate of decrease increases for higher C. The average EC temperature increases (for C = 1–450) and then decreases (for C > 450) because QEC follows the same trend.

At small irradiation concentrations, the membrane thickness appears to not be relevant for the operating current and only slightly affects the efficiency. For larger concentrations, the membrane thickness must be minimized in order for the device to operate under conditions of the Pareto front.

**Catalyst thickness.**—Here we discuss the effect of variation in the thickness (50-200 nm) of the two catalyst layers. The evolution of STH efficiency and Jop, S.5(e)-(d), shows that Jop insignificantly increases with increasing catalyst layer thickness. STH efficiency has its largest increase at C = 450, where its operating point is near the maximum power point of the PV. This concentration spans the largest operating current density change with varying catalysts thicknesses. The J-V curves, Fig. S.5(a)-(b), illustrate that the activation and concentration overpotentials decrease with almost no change in the ohmic losses when catalyst thicknesses are increased. Average PV and EC temperatures, Fig. S.5(e)-(f), are independent of catalyst thickness variations, mainly because the heat sources are insensitive to these thickness variations and because the reference flow velocity of the water (0.2 m/s) optimally removes the heat. The combined optimization of STH efficiency and Jop forms a Pareto frontier as shown in Fig. 7a, with the front comprised mainly of the thicker catalysts.

**Gas diffusion layer (GDL) thickness.**—The GDL thicknesses of both the anodic and cathodic sides were varied in the range of 300–800 μm. The evolution of Mвол shows that H₂ production decreases minimally with increasing GDL thickness (e.g. ~0.7% decrease for C = 124 with a thickness increase from 30 μm to 80 μm). STH efficiency follows the same behavior. However for the higher concentration range (C = 750–1000), the STH efficiency and hydrogen production remain constant with increasing GDL thickness. The J-V curves, Fig. S.6(a)-(b), show that the slope of the EC curve in the linear region decreases with an increase in GDL thickness, however the saturation current of the EC stays nearly the same. This implies that ohmic losses due to charge transport in the EC increase, whereas the saturation current of the EC doesn’t change with increasing GDL thickness. Additionally, no change in the activation overpotential was noticed. The average PV and EC temperatures, Fig. S.6(e)-(f), were found to be nearly independent of GDL thickness variations, primarily because the heat sources were found to be insensitive to this thickness variation at the chosen mean flow velocity of water, 0.2 m/s (optimized value). The combinations of C and GDL thickness which result in maximum STH efficiency (C = 1–150 and independent of GDL thickness) and H₂ production (C = 700–1000 and independent of GDL thickness) do not coincide, again forming a Pareto frontier, Fig. 7b. This front has no particular trend with respect to C but consists mainly of the smallest GDL thicknesses.

**Saturating behavior of performance parameters.**—Variation of the hydrogen production rate and STH efficiency with the investigated dimensional, operational, and material parameters is found to follow a saturating trend. This behavior is shown in Fig. 8 for C = 707.

The objective performance functions (Jop and STH efficiency) change somewhat significantly with an increase of the dimensional (GDL and catalyst layer thickness), material (ASSA and exchange current density), and operational (water velocity) parameters. Nevertheless, a saturation level is reached where any further increase in these parameters does not affect the performance. Mean flow velocity of 0.2 m/s, exchange current density of 30 times the reference value, ASSA of 10⁵ m⁻¹, catalyst thickness of 200 nm, and GDL thickness of 300 um optimize the performance of the integrated PEC device.

Figure 7. Operating STH efficiency for varying (a) anodic and cathodic catalyst thickness, (b) anodic and cathodic GDL thickness as a function of hydrogen production rate. The Pareto front is shown by the dotted black line. The color of the circles represents concentration and the color of the stars represents the (a) catalyst thickness and (b) GDL thickness.

Figure 8. Operating current density (left y-axis) and STH efficiency (right y-axis) as a function of GDL thickness, catalyst thickness, active specific surface area, exchange current density multiplier, and mean flow velocity, for the reference case I at C = 707.
Similar trends are observed at other irradiation concentrations, however the exact nature of the curve varies slightly.

Conclusions

We utilized our coupled 2-dimensional, non-isothermal multi-physics model\textsuperscript{17} to simulate the performance of an integrated PEC device utilizing concentrated irradiation. The model accounts for concentrated solar irradiation, electromagnetic wave propagation, semiconductor charge generation and transport, heat transfer, fluid flow, mass transport, electrolyte and electrode charge transport, and electrochemical reactions. Operation at large irradiation concentrations allows maximized hydrogen generation rates and increases the economic competitiveness of devices. The low fill factor of the PV cell and mass transport limitations of the electrochemical system put an upper limit on operating current for PV and EC area-matched devices, indicating an optimal irradiation concentration.

The J-V curves of the EC, with varying mass flow rates, intersect in a small potential region, giving rise to two distinctive regions of operation. Region I, corresponding to a low operating current density zone, is affected by temperature effects, leading to increasing slopes of the J-V curves of the EC for smaller temperatures. Region II, corresponding to a large operating current density zone, is characterized by mass transport limitations which lead to increased saturation currents of the EC with increasing mass flow rates. The formation of these two characteristic operational regions leads to trend reversals in the objective functions of STH efficiency and H\textsubscript{2} production when increasing the irradiation concentration. For any C, H\textsubscript{2} production and STH efficiency behave independent of the mass flow rate for mean flow velocities above 0.2 m/s. The maximum hydrogen production is achieved at $C = 700$–1000 and mean flow velocities between 0.1–2 m/s. The maximum STH efficiency is observed at $C = 1–30$ and doesn’t depend on the mass flow rate. The tradeoff between STH efficiency and $H_2$ production forms a Pareto front. This front consists of device configurations with the largest mean flow velocity. The effective cooling provided by the water channel on the top of the PV, with a mass flow rate of 40/g/s/m (equals a velocity of 0.2 m/s), is found to be optimal at all irradiation concentrations. Large water mass flow rates help in alleviating mass transport limitation and have better cooling capability than smaller rates.

Hydrogen production and STH efficiency increase for more active catalysts, i.e. increased exchange current density and active specific surface area (ASSA), at a particular C. $H_2$ production is maximized at large C while STH efficiency is maximized at small C. Consequently, a Pareto front exists which consists of cases with large exchange current density and large ASSA. Interestingly, at low and very large concentrations, the ASSA and exchange current density do not influence the performance, therefore the device performance is independent of any choice of catalyst substrate.

The membrane thickness is important for the performance of the integrated device, as its variation leads to significant changes in the operating points. The mass transport limitations are instigated earlier with increased membrane thickness, leading to reduced saturation currents. The large changes in operating current density with varying membrane thickness lead to significant changes in the EC and PV heat sources. However, the water mass flow rate ensures proper device cooling resulting in small temperature variations (a few Kelvin only). These minimal temperature variations, despite significant increases in heat sources, indicate functioning thermal management for the device. The largest $H_2$ production occurs at largest $C$ and thinnest membranes, whereas the maximum STH efficiency is observed at smaller concentrations ($C \leq 200$), and is found to be independent of membrane’s thickness. The objective functions of $H_2$ production and STH efficiency form a Pareto front which consists mainly of the cases with the thinnest membrane. The other dimensional properties, GDL and catalyst thicknesses, do not lead to significant changes in the operating point with parameter variations. The heat sources, and hence temperature, are found to be quite insensitive to these parameters. The Pareto front for these two cases consists mainly of the thinnest GDL and thicker catalyst.

The two objective functions show a saturating trend with increasing dimensional, operational, and material parameters. Mean flow velocity of 0.2 m/s (40/g/s/m), exchange current density of 50 times the standard value, ASSA of 10\textsuperscript{3}, catalyst thickness of 200 nm, and GDL thickness of 300 um were observed to be the optimum values for enhanced performance of the integrated PEC device for $C = 707$. Similar values are observed for other irradiation concentration factors.

Our 2-dimensional coupled multi-physics model allows for the investigation of any complex device design and geometry and simulation in fine physical detail. The model proves to be a valuable tool for the design of CIPEC devices working at elevated temperatures and highlights that smart thermal management assists in achieving efficient and low cost production of solar fuel at large rates. The results predict that thermal management can be used as a cost-effective and simple way of controlling device performance. For example, we predict that performance reduction due to degradation over the lifetime of the system can be controlled and counteracted by smart thermal management strategies: For operation at $C = 707$, a 12% degradation in STH efficiency can be compensated by a seven-fold increase in the mass flow rate. This benefit is observed for operational region I and II, although the strategy reverses depending on the region. Our results illustrate that smart thermal management – which is possible due to the integrated nature of our device design – allows for the development of CIPEC device operation, helps in the design of systems with prolonged high performance, ensures a performance advantage of integrated devices, and indicates that dedicated design and operation can circumvent limitations imposed by primary materials.

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List of Symbols

\begin{tabular}{|l|l|}
\hline
$C$ & Irradiation concentration (\(\mathrm{W/m^2}\)) \tabularnewline
$c$ & Speed of light (m/s) \tabularnewline
$E_\text{eq}$ & Equilibrium potential (V) \tabularnewline
$E_g$ & Bandgap of semiconductor (eV) \tabularnewline
$F$ & Faraday's constant (C mol\textsuperscript{-1}) \tabularnewline
$F_F$ & Fill factor of PV \tabularnewline
$h$ & Planck constant (J s) \tabularnewline
$I_a$ & Incident radiation flux (W/m\textsuperscript{2}) \tabularnewline
$i_{oc}$ & Local charge transfer current density (A/m\textsuperscript{2}) \tabularnewline
$J$ & Current density (A/m\textsuperscript{2}) \tabularnewline
$J_e$ & Electron current density (A/m\textsuperscript{2}) \tabularnewline
$J_h$ & Operating current density (A/m\textsuperscript{2}) \tabularnewline
$J_p$ & Hole current density (A/m\textsuperscript{2}) \tabularnewline
$J_i$ & Electrocatalyst current density (A/m\textsuperscript{2}) \tabularnewline
$J_e$ & Electrode current density (A/m\textsuperscript{2}) \tabularnewline
$J_s$ & Short circuit current density (A/m\textsuperscript{2}) \tabularnewline
$n_B$ & Boltzmann constant (J/K) \tabularnewline
$q_T$ & Total heat dissipation density (W/m\textsuperscript{3}) \tabularnewline
$Q_M$ & Magnetic losses (W/m\textsuperscript{3}) \tabularnewline
$Q_R$ & Resistive losses (W/m\textsuperscript{3}) \tabularnewline
$Q_{TH}$ & Thermalization losses (W/m\textsuperscript{3}) \tabularnewline
$\tilde{R}$ & Universal gas constant (Jmol\textsuperscript{-1}K\textsuperscript{–1}) \tabularnewline
$S_\text{av}$ & Time averaged Poynting vector (W/m\textsuperscript{2}) \tabularnewline
$T_{PV}$ & Average solar cell temperature (K) \tabularnewline
$T_{EC}$ & Average electrochemical cell temperature (K) \tabularnewline
$R$ & Net recombination rate in PV (1/m\textsuperscript{3}) \tabularnewline
$V$ & Potential/ Voltage (V) \tabularnewline
$V_{oc}$ & Open circuit voltage (V) \tabularnewline
$V_{mean}$ & Surface normal velocity of water (m/s) \tabularnewline
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References