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COMMUNICATION

Sunlight absorption in water – efficiency and design implications for photoelectrochemical devices

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Abstract: Sunlight absorption in water has a critical impact on solar fuel generation by direct photoelectrolysis because devices are commonly illuminated through the aqueous electrolyte. We show the relevant reference spectra, calculate fundamental solar-to-hydrogen efficiency potentials, and discuss the design implications for unassisted solar water-splitting devices.

The solar energy conversion efficiency of semiconductor devices underlies fundamental limitations related to discrete bandgaps and inevitable radiative recombination processes. Shockley and Queisser calculated the detailed balance limit for idealized photovoltaic (PV) cells based on single-junction absorbers.[1] Extensions to their approach derive fundamental efficiency prospects considering photochemical conversion (photolysis, photoelectrolysis),[2-4] the terrestrial solar spectrum,[2, 5] concentrated sunlight,[5] multijunction devices,[3-5] and multiple exciton generation.[3]
Since the discovery of solar photolysis,[6] intense experimental studies address renewable fuel generation by photoelectrochemical (PEC) water-splitting induced by sunlight absorption in semiconductors.[7] Tandem PEC devices, consisting of two[8] (or more[9]) series-connected absorber materials with different bandgaps, overcome the trade-off between insufficient voltage for unassisted water-splitting and insufficient utilization of the solar spectrum.[10] Despite continuous effort in modelling the solar-to-hydrogen (STH) conversion efficiency limits for PEC devices,[2, 3, 11] previous calculations rely on terrestrial solar irradiance data without considering illumination through an aqueous electrolyte, which is practically and principally inevitable for common device designs, including both conventional solid-state photoelectrode and alternative colloidal suspension systems.[12] Optical absorption in water is neither negligible nor independent of wavelength[13] – significant impacts on both the overall STH efficiency limits and the optimum design of PEC devices have to be expected.
In this Communication, we discuss the influence of light absorption in water on the performance prospect and device design for solar fuel generation. Our detailed balance calculations focus on tandem PEC devices for their superior performance potential[3] and dedication to high STH conversion efficiency[12], and reveal fundamental performance potentials in dependence of bandgaps, anticipated losses, and water film thicknesses.

Broader Context

Renewable energy research is of utmost importance for the development of a long-term, sustainable energy economy. Apart from limited global reserves, conventional energy supply largely based on fossil fuels produces excessive domestic greenhouse gas emissions responsible for global warming associated with unforeseeable risks and excessive societal costs. Solar and wind power have proven technological and economic feasibility, as well as generation potential relevant for the supply the fast-growing global energy consumption. Hydrogen as a chemical energy carrier is essential for energy storage, ammonia production, and as transportation fuel. Direct photoelectrochemical (PEC) hydrogen production aims to provide a clean, cost-effective, and locally produced solar fuel. High solar-to-hydrogen (STH) conversion efficiency is important for the commercial introduction of solar water splitting systems, emphasizing the necessity of tandem PEC devices for optimum use of the solar spectrum. However, sunlight absorption in the aqueous electrolyte has not previously considered as an influence factor although it can cause major energy loss and will reshape the solar spectrum. Our detailed balance calculations resolve the impact of illumination through water on STH efficiency prospects, and provide important guidelines for future PEC research on both device (bandgap combinations) and system design (allowable electrolyte thickness and overvoltage losses) levels.

We have calculated the transmittance of various water film thicknesses [Figure 1] based on the tabulated optical constants published by Hale and Querry,[14] supplemented by values of Palmer and Williams[15] for the near-infrared (IR) region. The spectral distribution of photon flux density after transmission through water [Figure 2] was determined based on AM1.5G spectral irradiance according to ASTM standard G173-3.[16] We used these as input for calculations of the STH efficiency prospects because pure water appears to be an appropriate lower limit of the absorbance of aqueous electrolytes during PEC operation. In detail, the detailed balance scheme[1, 5] was used to derive the idealized current-voltage characteristics $\boldsymbol{I(V)}$ for optically thick device structures. In analogy to Ref [3], we assume an electrical load consisting of the thermodynamic water-splitting potential ($\boldsymbol{E^0 = 1.23V}$) and a variable generalized overvoltage term ($\boldsymbol{V_O}$). The detailed balance limit of STH efficiency for the considered structure then directly relates to the derived water-splitting current $\boldsymbol{I_{H_2}(E^0 + V_O)}$:

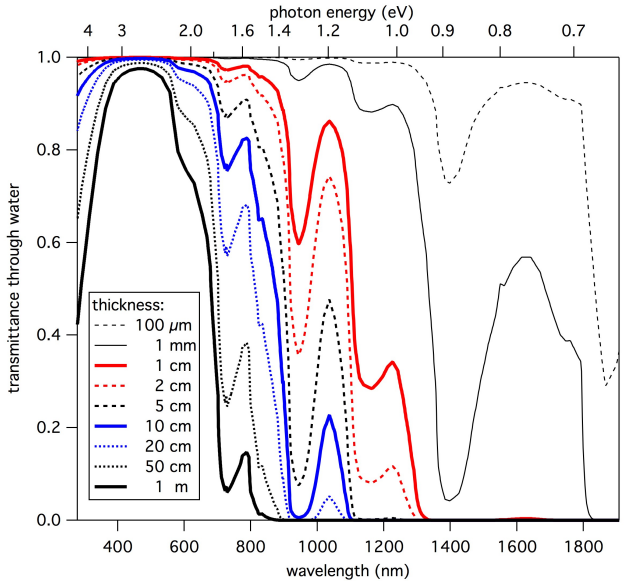

Figure 1: Optical transmission through water for various thicknesses.

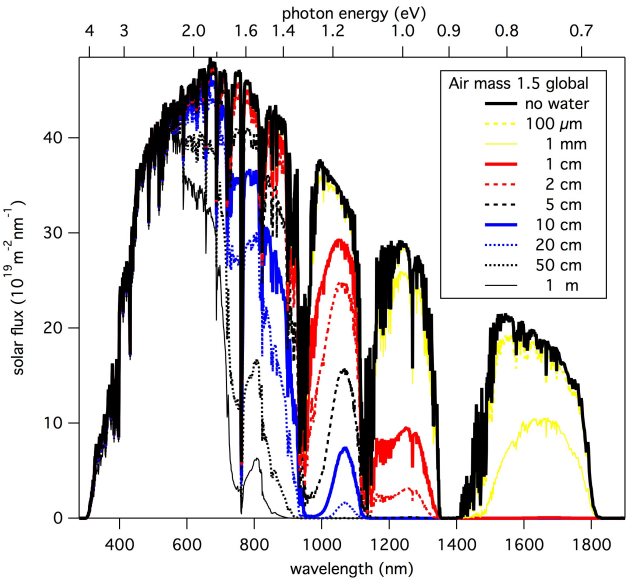

Figure 2: Terrestrial solar photon flux for global irradiance at air mass 1.5 according to standard ASTM G173-3 as well as flux after transmission through water films showing gradual loss for increasing thickness, particularly affecting higher wavelengths.

$$\eta_{STH} = \frac{p_{out}}{p_{in}} = \frac{I_{H_2} \cdot E^0}{p_{AM1.5G}}.$$

Note that the overvoltage term V_O accumulates any loss mechanisms due to imperfections throughout the whole, non-ideal, PEC system – besides fundamentally inevitable radiative recombination that is already covered within detailed balance. System imperfections include: non-radiative recombination channels and shunts impacting the $I(V)$ characteristics of the absorber; contacts and tunnel junctions (in tandems) causing resistive losses; kinetic overpotentials for hydrogen (HER) and oxygen (OER) evolution reactions; as well as the solution resistance of the electrolyte. Only the latter three factors alone result in a practical lower limit of $V_O \geq 400\ mV$ for an optimum conceivable PEC system[17] (with 20mA/cm^2 current density, Pt (80mV) and RuO_2 (220mV) co-catalysts, 100mV solution resistance loss. As a consequence, single-junction water-splitting device are confined to STH efficiencies below 17%[3] – not yet considering light absorption in the electrolyte.

Figure 1 shows the optical transmittance through water covering the wavelengths and thicknesses relevant for PEC. In typical laboratory configurations, PEC samples are illuminated through up to a few cm of electrolyte, where the transmission is beyond 95% for photon energies of 1.8 eV and above. Bandgaps for both explored (e.g., TiO_2) and idealized (2.0 eV[3]) single-junction devices fall in this range, and therefore, they should not significantly be affected by light absorption in water. However, the realization of STH efficiencies well above 15% will require tandem devices involving lower bandgaps[3] for better utilization of the solar spectrum. The current world-record PEC device,[8] an $GaInP_2$/GaAs tandem with 1.8-eV and 1.4-eV bandgaps, already suffers from some water-absorption losses. Further bandgap reductions—in particular, of the bottom bandgap—are necessary to access greater STH conversion prospects,[10] and careful consideration of sunlight absorption in the electrolyte will be inevitable.

Figure 2 displays the spectral distribution of the solar photon flux according to the standardized terrestrial global irradiance AM1.5G,[16] as well as its attenuation by transmission through water. The absorbed solar flux represents an upper limit of photocurrent density, important to estimate both the achievable hydrogen-generation rate and the current-matching within tandem PEC devices. The solar spectrum consists of several bands with increasing sensitivity to absorption in water with longer wavelength: All light beyond 1400 nm ($\leq 0.9\ eV$) is essentially lost during illumination through reasonably thick electrolyte layers. Sunlight around 1200 nm ($\leq 1.1\ eV$) quickly diminishes, too, but might still be relevant for PEC devices with minimal electrolyte films. Radiation around 1000 nm ($\leq 1.3\ eV$) will still contribute in typical laboratory-scale PEC setups (with 0.5–2 cm of electrolyte) with evident current loss compared to PV devices. Specific adjustments of PEC tandem structures will be necessary to maintain current-matched operation. Water transmission losses decrease further below 900 nm ($\geq 1.5\ eV$), but will still be problematic for proposed designs for PEC commercializtion[18] when involving a scale-up of the electrolyte thickness. Sunlight below 700 nm ($\geq 1.8\ eV$) is finally subject to rather negligible absorption levels. Note that alternative particle-bed PEC systems rely on distributed light absorption throughout an electrolyte suspension in the order of 10 cm.[12] Hence, absorber bandgaps and STH efficiency will essentially be restricted by the utilization of wavelengths below 900 nm.

We employed detailed balance calculations to quantify the effect of sunlight absorption on the performance prospects of PEC tandem device designs. Figure 3 shows exemplary contour plots of the STH efficiency limit in dependence of the bandgaps associated with the top and bottom junction, respectively. Fig. 3(a) shows an idealized device scenario without considering loss mechanisms associated with either overvoltage requirements or illumination through an electrolyte. The result agrees very well with ideal system (none but fundamental – i.e. radiative recombination – losses) cases previously published: Hanna and Nozik[3] predicted an optimum efficiency of 40.0% for a 1.40-eV and 0.52-eV bandgap combination; Bolton et al.[2] also arrived at about 40% with slightly different bandgaps based on older spectral irradiance data. Part (b) displays significant changes associated with sunlight absorption in an electrolyte based on device illumination through a 2-cm-thick water film. The theoretical maximum for STH conversion efficiency drops significantly to just 24.6% without consideration of any overvoltage loss. The result is explained by the near total loss of photon flux for wavelengths beyond 1100 nm (see Figure 2). The loss is even more dramatic for the optimum bandgap combination from Fig. 3(a):

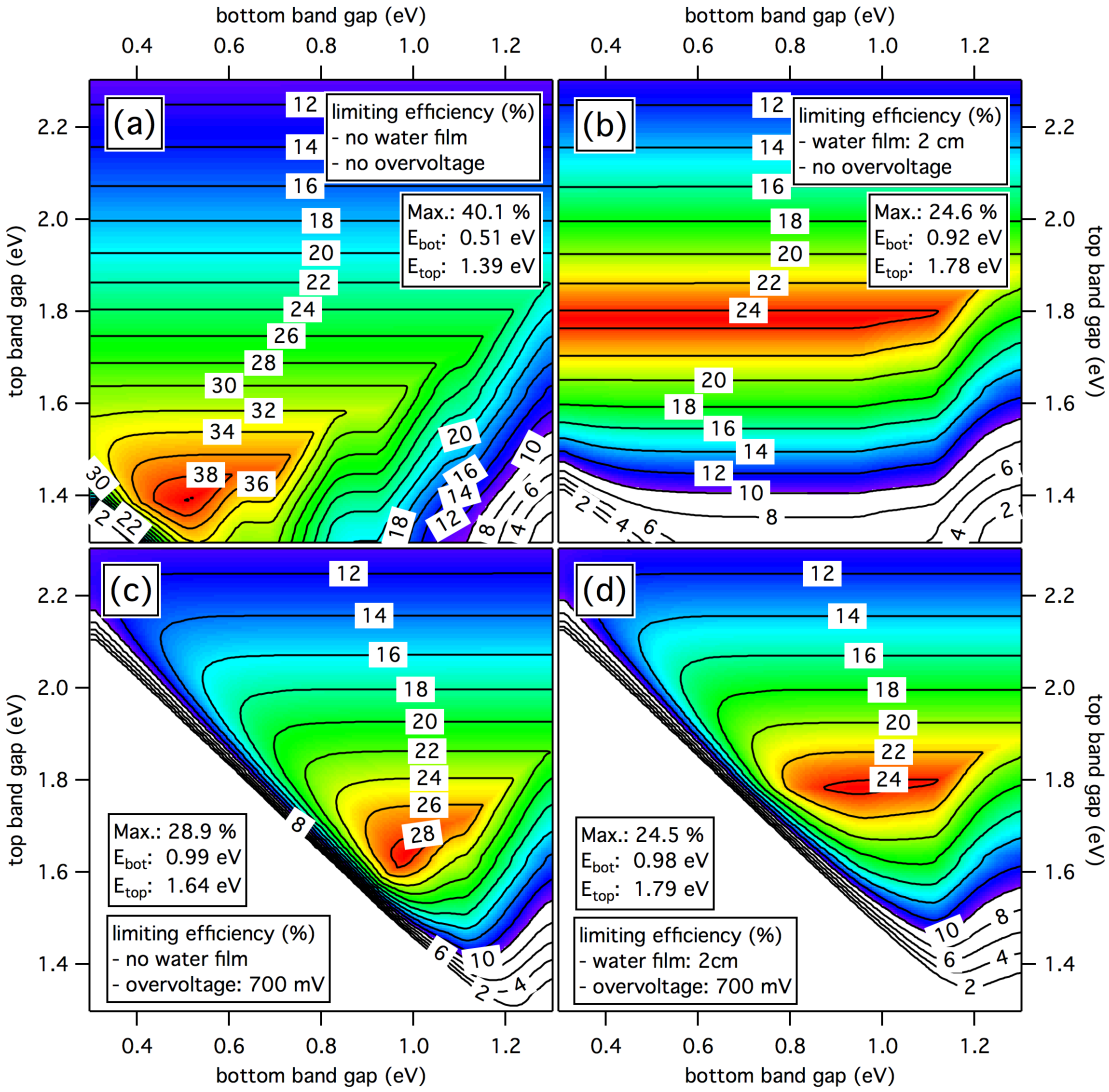

Figure 3: Maps of theoretical tandem PEC efficiency limits over the bandgap energies of bottom and top junction, for (a) idealized case without both water coverage and overvoltage, (b) under 2 cm of water, without consideration of overvoltage, (c) an overvoltage of 700 mV, without consideration of water coverage, and (d) for realistic PEC operation under 2 cm of water and assuming 700 mV of overvoltage loss.

Illuminated through the electrolyte, this device would suffer extremely from current limitation by the bottom junction, leading to an STH efficiency limitation below 10%. Accordingly, an increase of the top-junction bandgap from 1.39 eV (a) to 1.78 eV (b) is necessary to leave enough light for a current match of the bottom junction. In contrast, the STH performance prospects appear to be basically independent of the chosen bottom bandgap. Unlike PV efficiency, where maximum device power depends on the trade-off between current density and output voltage, the hydrogen-generation rate of PEC devices—and therefore, their efficiency—is directly proportional to their current. Given sufficient potential to drive the water-splitting reaction, a further increase of voltage is irrelevant unless driving a higher hydrogen generation current. In this light, it also appears worthwhile to reconsider the general superiority of tandem PEC devices over single-junction devices[3] for realistic illumination through an electrolyte (see below).

Figure 3(c) shows the established STH efficiency prospects of tandem PEC devices affected by overvoltage[3, 11] for a more realistic exemplary scenario of 700 mV (i.e. including an arbitrary 300 mV tolerance for solid-state deficiencies, alternative co-catalysts, etc.). The result is similar to Hu et al.[11] who obtained a limit of 29.7% for a 1.60/0.95 eV combination (in a model assuming specific loss levels). No matter whether consumed by kinetic overpotentials, by solution resistance, by non-radiative recombination, or by other non-ideal system deficiencies, overvoltage sums up additional potentials to be overcome to split water. Basically, this translates to higher bandgaps for both junctions (balanced to maintain current-matching), sacrificing output current and efficiency prospects for higher voltage to actually split water. Note that Fig. 3(c) in principle equals Fig. 3(a) except for a significantly increased cut-off, where STH efficiency drops quickly to zero for insufficient voltage to split water. Finally, Figure 3(d) displays a more realistic scenario for the detailed balance limit of STH efficiency unifying the constriction of both illumination through water and overvoltage for 2 cm and 700 mV, respectively. Although the overvoltage induces the same cut-off conditions as in Fig. 3(c), both optimum STH efficiency potential and the associated bandgap combination equals Fig. 3(b): The main difference is that additional voltage gained by the choice of a higher bandgap for the bottom junction is now actually required to overcome overvoltage loss.

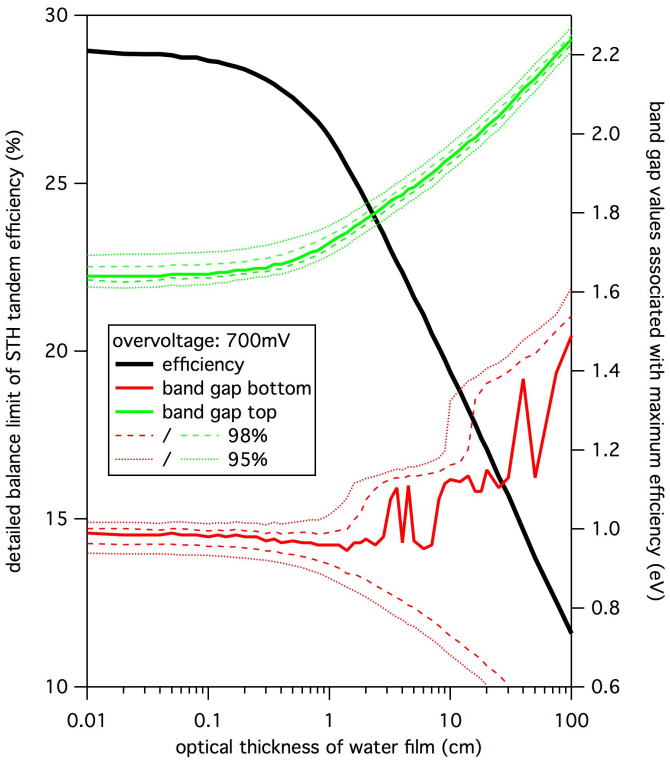

Figure 4: Theoretical STH efficiency limit of a PEC device with an overvoltage loss of 700 mV over thickness of the water film (black line) as well as the associated bandgaps of the top (green) and bottom (red) junction including margins for 98% (dashed) and 95% (dotted) of maximum performance.

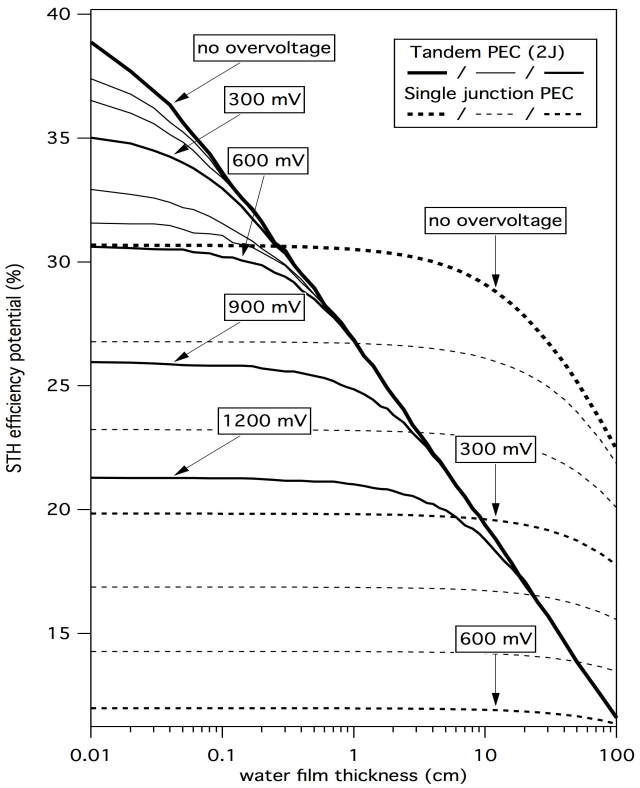

Figure 5: Theoretical STH efficiency limit efficiencies of 2-junction tandem (solid lines) and single-junction (dashed lines) PEC devices plotted over the thickness of the water film used during operation. Applicable overvoltage losses are indicated.

Apparently, both illumination through an electrolyte and overvoltage represent rigorous limitations for the STH efficiency prospects of PEC devices. Nevertheless, the results in Figure 3 seem to indicate that a certain level of overvoltage loss does not represent a further restriction to the PEC device performance when illumination through a given electrolyte thickness is given – and vice versa. We tested this hypothesis by calculating the detailed balance limit of STH efficiency for a PEC tandem configuration with 700 mV for various illumination conditions. The results in term of maximum STH performance prospects and associated bandgap energies for both junctions are depicted in Figure 4 over several orders of magnitude of water film thickness.

Illumination through negligible water layers obviously represents the scenario presented in Figure 3(c), where STH efficiency is limited at about 29% by the overvoltage demand of 700 mV. Although a few mm of water drastically diminish the IR portion of the solar flux (Figure 2), the hydrogen-generation prospect remains nearly unaffected because the device requires a higher-energy absorption edge of the bottom junction anyway to supply sufficient voltage to drive the water-splitting reaction. Illumination through water films of 1 cm and beyond goes along with a continuous decrease of STH efficiency prospect. In parallel, the optimum bandgap of the top junction rises significantly, notably not to provide a higher voltage, but exclusively to leave sufficient photon flux for current-matched operation with the bottom junction. In Figure 4, lines associated with 98% (dashed) and 95% (dotted) of the maximum STH efficiency for a given water film thickness indicate the sensitivity of hydrogen generation rate on the actual choice of top and bottom bandgap. Similar to the observation in Figure 3(b), the energy of the bottom junction becomes increasingly irrelevant beyond 1 cm of water.

Figure 5 displays the detailed balance STH efficiency limit over water film thickness as well as its dependence on overvoltage for both single-junction and tandem PEC devices. In general, all traces for tandem STH efficiency follow the same pattern discussed for Figure 4: Each begins at a characteristic maximum determined by the assumed overvoltage, stays nearly constant until the water film thickness exceeds a certain value, where the transmission loss during illumination begins to affect the current-matching of the bottom junction. In general, the calculation for no overvoltage represents an envelope to which the tandem efficiency for any given overvoltage will asymptotically approach for high-enough electrolyte thicknesses.

In comparison to tandems, single-junction PEC devices require materials with higher bandgaps. Hence, their STH efficiency prospects are both limited to lower values,[3] but also less affected by light absorption in the electrolyte. As shown in Figure 5, limiting efficiencies remain fairly constant up to 10 cm and beyond. Therefore, an extended regime of water film and overvoltage combinations exists, where the STH efficiency potential of single-junction PEC devices exceeds that of tandem structures. The observation might be of limited practical relevance though, because the sensitivity of single-junction PEC efficiency to overvoltage loss is much worse than for tandem structures.† Since 400 mV represents a lower limit of conceivable overvoltage for PEC operation (see above), the STH efficiency prospects for single-junction devices are already limited to about 15% – and will only beat the performance limit of tandems when illuminated through 20 cm of water or more. Techno-economic analysis[12] clearly shows that different configurations will be necessary to provide hydrogen as a competitive solar fuel.

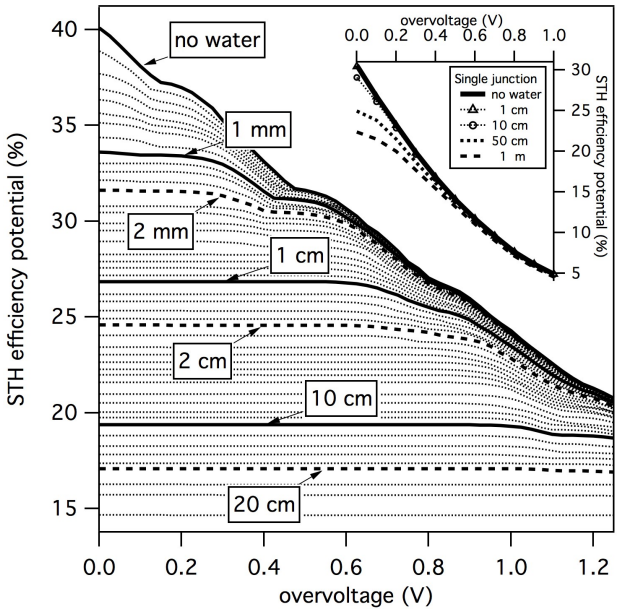

Figure 6: Theoretical STH efficiency limit for 2-junction tandem PEC device operation under various water layer thickness over overvoltage loss. The inset shows analogous calculations for single-junction PEC devices.

Addressing the clear need for high-efficiency tandem PEC devices beyond the current world-record $GaInP_2/GaAs$ configuration,[8] fundamental PEC research will require a dedicated search for materials combinations not only reflecting optimum bandgaps (according to boundary conditions to be determined in line with Figures 3–5), but also, providing sufficient material quality to actually come close to the limiting STH efficiencies derived by our calculations. Promising research directions will be the epitaxial integration of a higher (1.7–1.9-eV) bandgap material on Si (1.12 eV)[10] or the use of modern inverted metamorphic (IMM) III-V growth techniques[19] for PEC—in particular, to combine high-performance $GaInP_2$ (1.81 eV) with a bottom-cell material (1.0–1.2 eV) for current-matched water-splitting operation.
Simultaneously, applied PEC research needs to address system designs for the scale-up toward technological and economical implementation. Proposed designs need to be re-evaluated regarding transmission loss during illumination through the electrolyte. The representation of our STH detailed balance calculation in Figure 6 is meant to provide some basic guidelines: With a practical lower limit of 400-mV overvoltage loss, research toward ultra-high-efficiency PEC devices might actually aim for about 30%, in case innovative system designs with thinnest (< 1 mm) electrolyte films or "dry" back-side illumination were applied. On typical laboratory scales (with 1–2 cm of electrolyte), the STH efficiency potential is limited to about 25%; in turn, catalyst choices toward a total level of overvoltage losses of 600–800 mV are actually tolerable without a major direct impact on performance. Finally, the design of large-scale PEC technology[18] needs to address the issue technologically of sufficient electrolyte thickness. Just 10 cm will already decrease the STH efficiency limit below 20%. Here, the importance of systems engineering toward less electrolyte significantly outweighs any co-catalysis issues. For systems requiring illumination through even thicker electrolyte layers, including nanoparticle-suspension PEC systems,[12] single-junction devices might also be interesting provided overvoltage loss could be strictly limited.

Conclusions

Sunlight absorption in aqueous electrolytes significantly affects the performance of PEC water-splitting devices based on the solid-liquid junction on the semiconductor surface—in particular, of high-efficiency tandem structures intended for better utilization of the solar spectrum. Our detailed balance calculations considering illumination through water as a lower limit for the transmission loss in electrolytes predict the STH efficiency potential for idealized single-junction and tandem PEC devices with arbitrary bandgap combinations. The results differ significantly from previous calculations[2, 3, 11] that strictly neglected sunlight absorption in the electrolyte: Only 2cm of water already diminish the STH conversion efficiency of an ideal PEC system (none but radiative losses) from above 40% to less than 25%, achievable with a very different bandgap combination. Hence, our calculations provide new impulses for the design of dedicated PEC device structures. The most important observation is a close relation between implied overvoltage losses and allowable electrolyte thickness that will be a crucial design parameter for scale-up of PEC systems towards an economically viable source of solar fuel.

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Notes and references

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† Note that overvoltage in a realistic tandem configuration will be higher than in a single-junction case due to additional loss associated with the tunnel junction and a second non-ideal absorber. All solid-state deficiencies are still neglected in the 400mV practical lower limit.

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