Counter-balancing light absorption and ionic transport losses in the electrolyte for 1 integrated solar water splitting with III-V/Si dual-junctions 2 Moritz Kölbach,¹ Ciler Özen,² Oliver Höhn,³ David Lackner,³ Markus Feifel,³ Fatwa 3 F. Abdi,² and Matthias M. May^{1, a)} 4 ¹⁾Universität Ulm, Institute of Theoretical Chemistry, Lise-Meitner-Str. 16, 89069 Ulm, 5 Germany ²⁾Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 7 Institute for Solar Fuels, Hahn-Meitner-Platz 1, 14109 Berlin, 8 Germany 9 ³⁾Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstraße 2, 79110 Freiburg, 10 Germany 11 (Dated: 31 July 2021) 12 Recently, significant progress in the development of III-V/Si dual-junction solar cells has 13 been achieved. This not only boosts the efficiency of Si-based photovoltaic solar cells, 14 but also offers the possibility of highly efficient green hydrogen production via solar water 15 splitting. Using such dual-junction cells in a highly integrated photoelectrochemical ap-16 proach and aiming for upscaled devices with solar-to-hydrogen efficiencies beyond 20%, 17 however, the following frequently neglected contrary effects become relevant: (i) light ab-18 sorption in the electrolyte layer in front of the top absorber and (ii) the impact of this layer 19 on the ohmic and transport losses. Here, we initially model the influence of the electrolyte 20 layer thickness on the maximum achievable solar-to-hydrogen efficiency of a device with 21 an Si bottom cell and show how the top absorber bandgap has to be adapted to minimise 22 efficiency losses. Then, the contrary effects of increasing ohmic and transport losses with 23 decreasing electrolyte layer thickness are evaluated. This allows us to estimate an optimum 24 electrolyte layer thickness range that counterbalances the effects of parasitic absorption 25 and ohmic/transport losses. We show that fine-tuning of the top absorber bandgap and the 26 water layer thickness can lead to an STH efficiency increase of up to 1% absolute. Our re-27 sults allow us to propose important design rules for high-efficiency photoelectrochemical 28 devices based on multi-junction photoabsorbers. 29

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Hydrogen produced from water and sunlight offers the potential to significantly contribute to 30 the decarbonisation of the energy sector on a global scale.^{1,2} One possible route towards solar 31 hydrogen is photoelectrochemical (PEC) water splitting. In short, a dual-junction photoabsorber 32 immersed in an electrolyte captures the incident sunlight, generates a photocurrent as well as a pho-33 tovoltage, and drives the oxygen and hydrogen evolution reactions at the respective semiconductor-34 electrolyte interfaces. Despite decades of research, however, no material system was demonstrated 35 that fulfils all of the following requirements for a commercially viable PEC system: (i) a lifetime 36 on the time scale of years, (ii) high abundance of the absorber and catalyst materials, and (iii) a 37 high solar-to-hydrogen (STH) efficiency. The latter is especially important, since efficiency be-38 comes a key factor determining the hydrogen production cost, when the balance of system (BOS) 39 and land costs shift away from the materials costs. Moreover, techno-economic analyses imply 40 that only highly efficient PEC water splitting might compete with the technological more mature 41 approach of powering an electrolyser by photovoltaics via the grid.³ The current record PEC de-42 vice with respect to efficiency is based on a GaInP/GaInAs dual-junction cell, reaching 19% STH.⁴ 43 However, the relatively low stability and the high-cost of the required GaAs-substrate are currently 44 preventing practical applications.^{5,6} 45

One possible way to significantly reduce the cost of III-V-based devices is to replace the GaAs-46 substrate with Si that also acts as a bottom absorber.^{6–8} Indeed, demonstrated efficiencies of III-47 V/Si multi-junction photovoltaic solar cells have significantly increased in the recent years. Also 48 for integrated solar water splitting, there has been an increased interest for this approach over the 49 last years.^{8,9} In 2018, Cariou et al. achieved a photovoltaic conversion efficiency of 33.3% with 50 a wafer-bonded two-terminal GaInP/GaAs//Si solar cell under AM1.5G illumination, which was 51 further improved to 34.1%.^{7,10} Only recently, a new record of 35.9% was achieved using a wafer-52 bonded two-terminal GaInP/GaInAsP//Si cell.¹¹ Direct growth of the III-V cell(s) on top of a Si 53 bottom cell offers potential cost and scalability benefits, but is also more challenging due to defects 54 at the III-V/Si interface, which is why achieved efficiencies are still lower than those reported for 55 the wafer-bonding approach.^{12,13} These developments pave the way for the development and fabri-56 cation of III-V/Si dual-junction cells for solar water splitting that promise similar high efficiencies 57 as recent PEC record devices. Moreover, there has been significant progress in Perovskite/Si 58 dual-junction devices^{14,15}, which are also considered potential candidates for highly efficient so-50 lar water splitting. It should, however, be noted that the longterm stability of direct or integrated 60 approaches is still a major challenge that needs to be addressed before III-V/Si or Perovskite/Si 61

⁶² photoelectrochemical dual-junction cells can reach large-scale commercial applications.¹⁶

With STH efficiencies above 20% within reach, a number of effects become relevant that are 63 frequently neglected in lower-efficiency devices, but cannot be ignored when approaching the 64 physical limits. In a dual-junction, two-terminal cell, the two absorbers are connected in series 65 and the overall efficiency is determined by the absorber with the lowest current (current match-66 ing). Hence, the efficiency is highly sensitive to changes in the solar spectrum. In any PEC 67 device, the incident light has to pass through a – typically aqueous – electrolyte before reaching 68 the absorber. Since water absorbs near-infrared light, the effective illumination spectrum onto the 69 cell deviates from the AM1.5G spectrum. Efficiency losses are therefore unavoidable and can be 70 even more emphasised when the bandgaps of the multi-junction cells are perfectly matched to 71 the AM1.5G spectrum instead of to the effective spectrum.^{16–19} An obvious strategy to minimise 72 the parasitic absorption in the electrolyte is to decrease the water layer thickness in front of the 73 absorber. However, with decreasing electrolyte thickness, ohmic and transport losses may in-turn 74 decrease the efficiency representing a typical non-linear optimisation problem, leading to a global 75 maximum of the theoretical efficiency as a function of the electrolyte layer thickness. Due to the 76 current-matching condition in a monolithic dual-junction, this will then directly impact the ideal 77 bandgaps of the photoabsorbers. 78

In this work, we deconvolute the effects of the electrolyte layer thickness on the efficiency of 79 a III-V/Si dual-junction device. Therefore, we initially investigate the influence of the electrolyte 80 layer thickness on the maximum achievable solar-to-hydrogen efficiency and show how the top 81 absorber bandgap has to be adapted to minimise efficiency losses under idealised conditions. Next, 82 we model the ohmic and transport losses with decreasing electrolyte layer thickness. We use 83 experimental III-V//Si dual-junction device data (as the performance target for directly grown III-84 V/Si) and combine the effects of parasitic absorption and ohmic/transport losses. We hereby show 85 that fine-tuning of both the top absorber bandgap and the water layer thickness can enable an 86 absolute STH efficiency increase of up to 1%. 87

Fig. 1(a) shows a sketch of a monolithic dual-junction PEC device with Silicon as a bottom absorber, indicating the near-infrared light absorption in the electrolyte under AM1.5G illumination. The effective spectra that reach the cell as a function of the water layer thickness in the relevant wavelength-range ($E_{g,Si} = 1.1 \text{ eV}$, i.e. 1127 nm) is shown in Fig. 1(b). Even a thin water layer of 0.3 cm decreases the effective intensity for wavelengths > 980 nm. When the water layer thickness is 5 cm, the intensity is drastically decreased for wavelengths > 700 nm. The absorption ⁹⁴ coefficient stays finite also for lower wavelengths,²⁰ but the effect becomes negligible as water
⁹⁵ layers of serveral cm are practically not reasonable, also due to the resulting weight of the device.
⁹⁶ However, it emphasises the need for a reliable benchmarking protocol for the characterisation of
⁹⁷ PEC multi-junction devices in the lab.²¹



FIG. 1. (a) Sketch of a dual-junction cell for PEC solar water splitting indicating the absorption of the incident light in the electrolyte. (b) Effective AM1.5G spectra (reference data from the American Society for Testing and Materials²²) modified by the water layer (absorption data from Refs.^{20,23}) with different thicknesses hitting the top absorber of the dual-junction cell. (c) STH efficiencies modelled for an ideal case as a function of the water layer thickness and the top absorber bandgap from the detailed balance limit and Pt- and IrO_x -catalyst characteristics without thinning of the top absorber, and (d) with optimal thinning. (e) Maximum achievable STH efficiency for a fixed (dashed lines) and optimised (solid lines) top absorber bandgap as a function of the water layer thickness. The ohmic cell resistance is assumed to be constant in all calculations (i.e. water layer thickness-independent).

To initially only assess the influence of light absorption in the electrolyte layer on the device efficiency, a constant (i.e. water layer thickness-independent) ohmic cell resistance is assumed in our calculations shown in Figs. 1(c), 1(d), and 1(e). This ideal case scenario is modelled with our

open-source Python package YaSoFo²⁴ is based on the following conditions: highly efficient Pt-101 and IrO_x catalysts (see Figure S1 for IV-characteristics), neglected concentration overpotentials, 102 open circuit voltages obtained from the detailed balance limit, IV solar cell characteristics follow-103 ing the single diode equation, and an operating temperature of 25 °C (see SI Table S1 for full list 104 of input parameters and the YaSoFo documentation for full model description²⁴). Fig. 1(c) shows 105 the STH efficiency as a function of the top absorber bandgap and the water layer assuming that all 106 photons with an energy higher than the bandgap are absorbed and contribute to the photocurrent. 107 The same plot in which the thickness of the top absorber is allowed to be optimised from growth 108 to be not fully absorbing (i.e. "thinned"), so that more photons can reach the Si bottom absorber 109 to ensure current matching conditions is shown in Fig. 1(d). The maximum theoretical efficiency 110 decreases with increasing water layer thickness from 26.9% (0.1 cm), 26.3% (0.4 cm), and down to 111 18.9% (10 cm). This represents an intrinsic efficiency loss in the photoelectrochemical solar water 112 spitting approach. The red dashed line in Fig. 1(e) shows the higher efficiency losses, when the 113 top absorber bandgap is not adapted to the water layer thickness (blue dashed line). Interestingly, 114 Figs. 1(c) and 1(d) imply that there are two ways to minimise these losses and reach the maximum 115 theoretical efficiency: (i) decrease the thickness of the top absorber so more photons can reach the 116 Si bottom absorber, or (ii) increase the bandgap of top absorber (solid blue line in Fig. 1(e). While 117 both approaches have the same maximum achievable efficiency for a given catalyst performance, 118 the latter would increase the photovoltage allowing for higher ohmic losses in the device, or the 119 use of less catalyst loading or catalysts with a lower activity, respectively. 120

To model the influence of the water layer thickness on the voltage losses, we used a simplified 121 2-D cell geometry as shown in Fig. 2(a). The calculations assume a stagnant 1 M HClO₄ elec-122 trolyte, a more realistic operation temperature of 40 °C, no membranes, and anodes that are placed 123 on the sides of the cell. Note that this highly idealised cell geometry does not represent a practical 124 water splitting device (e.g. no safe product separation). However, it gives a first impression on the 125 voltage losses associated with a thin water layer. Note that the size of the gas bubble plume²⁵ cre-126 ates another boundary condition for the minimum thickness of the water layer, but this is currently 127 neglected in the model. To asses the ohmic losses and concentration overpotentials in the cell, the 128 steady-state conservation, Nernst-Planck (diffusion and migration), as well as the concentration-129 dependent Butler-Volmer equation were solved employing the finite element method in COMSOL 130 Multiphysics (see SI supplementary note 1 and Table S2 for more details and input parameters, 131 respectively). 132



FIG. 2. (a) Sketch of the idealised 2-D cell geometry used for the modelling indicating the dimensions and arrangement of the cathode, the anodes, and the electrolyte. (b) Sum of the ohmic and concentration voltage losses for a constant current density of 15 mA/cm^2 as a function of the cathode size simulated with COMSOL. (c) Respective calculations varying the current density for a constant cathode size of 4 cm. The individual contributions of the ohmic and concentration losses are shown in the SI Figure S2.

As expected, our calculations show that the voltage losses (sum of the ohmic and concentration overpotentials) increase with decreasing electrolyte thickness and increasing cathode size (see Fig. 2a). This is caused by the reduced cross-section of the conductive water layer leading to higher ohmic losses and mass-transport limitations. For example, the voltage loss doubles from 51 mV to 106 mV while decreasing the water layer thickness from 1 cm to 0.1 cm for a fixed current density of 15 mA/cm² and a cathode size of 4 cm. For smaller cathode sizes, the voltage losses also double, but the absolute losses are lower. These results emphasise the need for PEC



FIG. 3. (a) IV characteristics under AM1.5G illumination of a AlGaAs//Si solar cell prepared by wafer bonding measured in the Fraunhofer ISE CalLab. (b) Sum of the EQEs of the two subcells measured at Fraunhofer ISE CalLab. (c) STH efficiencies modelled by YaSoFo²⁴ as a function of the water layer thickness and the top absorber bandgap assuming a constant voltage loss. (d) Extracted maximum efficiency and the associated top absorber bandgap. (e), (f) Respective calculations considering the voltage losses modelled with COMSOL shown in Fig. 2(c) for a cathode size of 4 cm. All calculations were performed without the possibility of top absorber thinning. Full list of input parameters and the resulting 2-electrode water splitting IV characteristics are shown in the SI Table S1 and Figs. S3/S4, respectively.

device configurations that allow short ion path lengths. Since the absolute voltage losses increases with increasing cathode size, this is especially important for upscaled devices. The influence of the current density shown in Fig. 2(c) also reveals the expected trend: The voltage losses increase with increasing current density and decreasing water layer thickness. For a cathode size of 0.4 cm, the voltage loss increases from 58 mV to 116 mV with decreasing water layer thickness from 1 cm to 0.1 cm for a current density of 20 mA/cm². Note that the individual contribution of ohmic and concentration losses are similar in the considered parameter space (see SI Figure S2).

In order to determine the optimal condition, we now combine the two effects of the electrolyte layer: parasitic light absorption and the voltage losses caused by the ohmic and concentration

overpotentials. For a more realistic analysis, experimental state-of-the-art III-V//Si dual-junction 149 device data instead of the previously employed detailed balance limit is used. Figs. 3(a) and 3(b) 150 show the IV characteristics under AM1.5G illumination and the external quantum efficiency (EQE) 151 spectrum of an AlGaAs//Si solar cell, respectively. The AlGaAs top absorber ($E_g = 1.75 \text{ eV}$) 152 was joined with the Si bottom absorber via wafer bonding resulting in photovoltaic conversion 153 efficiencies of up to 29.1% (see Ref.¹⁰ for experimental details). In the calculations shown in 154 Fig. 3(c-f), the experimental IV and EQE data is used as an input to inter alia account for par-155 asitic absorption, recombination losses, as well as ohmic and finite shunt resistances in the ab-156 sorber (see supplementary note 2 and Table S1 for full list of input parameters). The assumed 157 operating temperature of 40 °C is implemented via the temperature coefficient of the open circuit 158 voltage. Note that for an even more realistic device modelling, the optics of the total stack (i.e. 159 air/window/water/catalyst/protection layer/absorber) as well as the exact cell geometry would have 160 to be considered. However, this is out of the scope of the current study and is left for future work. 161 Fig. 3(c) shows the STH efficiency based on the experimental AlGaAs//Si cell characteristics as 162 a function of the top absorber bandgap (no thinning) and the water layer thickness without taking 163 the additional voltage losses due to a thinner water layer into account. The extracted maximum 164 STH efficiency and the associated top absorber bandgap is illustrated in Fig. 3(d). As expected, the 165 calculations show a similar trend as those shown in Fig. 1(c) based on the detailed balance limit. 166 However, a lower maximum STH efficiency of 20.5% is achieved for the smallest considered wa-167 ter layer of 0.1 cm. Figs. 3(e) and 3(f) show the respective calculations considering the additional 168 voltage losses caused by the thinned water layer from Fig. 2(c). The effect is clearly visible. The 160 overall maximum achievable STH efficiency has shifted away from the lowest considered water 170 layer thickness of 0.1 cm to a value of around 0.7 cm. In this thickness region, the effects of the 171 parasitic absorption and voltage losses are counterbalanced. Figs. 3(e) and 3(f) reveal the impor-172 tant conclusion that fine-tuning of both the top absorber bandgap and the water layer thickness can 173 lead to an absolute STH efficiency increase in the order of 1%. 174

Another parameter that influences the trade-off between parasitic light absorption and ion transport losses in the water layer, which was not discussed until now, is the 2-electrode water splitting catalyst performance (see Fig. 4). In the model, the catalyst performance was varied by changing the exchange current density of the OER catalyst (x-axis), while keeping the exchange current density of the HER catalyst constant. The resulting kinetic overpotential to achieve a 2-electrode water splitting current density of 20 mA/cm² is indicated on the upper x-axis as a more tangible

value. The red and blue solid lines show the optimised water layer thickness (left y-axis) and 181 the corresponding overall maximum STH efficiency (right y-axis) as a function of the catalyst 182 performance, respectively. For clarification, these values correspond to the maximum of the STH 183 efficiency vs. water layer thickness plot shown in Figure 3(f). Note that each optimised water layer 184 thickness also has a corresponding optimised top absorber bandgap (not shown). Furthermore, the 185 distribution of the current density flowing in the electrolyte is assumed to be not affected by the 186 exchange current density (i.e. the voltage losses shown in Fig. 2(c) are independent of the catalyst 187 performance). 188

When the overall efficiency is limited by current matching in the dual-junction cell and not 189 by the catalysis, the solar cell generates more voltage than required (larger top absorber bandgap 190 to allow more photons to reach the Si bottom absorber). In other words, the system operates at 191 potentials below the MPP of the solar cell. This extra voltage, which is otherwise transformed into 192 heat, can be used to counterbalance the voltage losses caused by a thin water layer (see Fig. 2). 193 Hence, maximum STH efficiencies are reached at low water layer thicknesses due to a lower 194 parasitic absorption for a very good catalyst performance (right-hand side of Fig. 4). If, on the 195 other hand, the catalyst performance is limiting and defines the magnitude of the top absorber 196 bandgap, every additional ion transport voltage losses will lower the maximum achievable STH 197 efficiency. Hence, the maximum efficiency is reached at elevated water layer thicknesses. Note 198 that for a realistic device, it is more likely that the catalyst performance will be the limiting factor. 199 For comparison, the dashed blue line shows the respective maximum STH efficiency when the 200 water layer is fixed, i.e. not adapted to a reduced catalyst performance (dashed red line). The 201 maximum achievable efficiency gains are again in the order of 1% (absolute), when the water 202 layer is optimised with respect to the catalyst performance. 203

In summary, we modelled and deconvoluted the effect of the water layer on the maximum 204 achievable STH efficiency of a III-V/Si dual-junction device for PEC solar water splitting. We 205 showed that fine-tuning of both the top absorber bandgap and the water layer thickness to coun-206 terbalance the effects of parasitic absorption and voltage losses can lead to an STH efficiency 207 increase of up to 1%. Moreover, our study emphasises the need to explore device designs that 208 minimise the ohmic and transport losses associated with a thin water layer. This work lays the 209 foundation for the development of a realistic PEC device model. Extending our calculations with 210 experimentally obtained optical properties of the total stack (air/window/water/catalyst/protection 211 layer/absorber), a practical and upscaled cell geometry, and including the influence of convection 212



FIG. 4. Water layer thickness (red solid line) for which the overall maximum STH efficiency (blue solid line, right y-axis) is achieved as a function of the OER exchange current density used as an figure of merit for the overall 2-electrode catalyst performance. The top x-axis indicates the kinetic overpotential to achieve a 2-electrode water splitting current density of 20 mA/cm². The blue dashed line represents the respective maximum efficiency values for a fixed water layer of 0.1 cm.

will be the subject of follow-up work. From a broader perspective, our results give important
insights into the challenges of designing any highly efficient multi-junction PEC system, also
beyond solar water splitting.

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220 DATA AVAILABILITY

The base code used for this study is available open source on the Zenodo repository under DOI:10.5281\zenodo.1489157, specialised functions used here will be made available upon publication of the manuscript. All further data, including the description of the model and all the input parameters, is available in the supplementary materials.

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