Beyond Water Splitting: Efficiencies of Photo-Electrochemical Devices Producing Hydrogen and Valuable Oxidation Products

Mei, Bastian ; Mul, Guido; Seger, Brian

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Supporting Information

**Beyond water splitting - efficiencies of photoelectrochemical devices producing hydrogen and valuable oxidation products**

Bastian Mei, a,* Guido Mul, a Brian Segerb,*

**Experimental**

The parameter set used to model the devices presented in the main article is shown in Table S1. The precision options used are shown below.

### Table S1. Simulation parameters for the modelling of the electrochemical parameters of hydrogen HER, bromine BrER, and chlorine ClER evolution reaction.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>t</td>
<td>Water film thickness</td>
<td>2 cm (0 cm)</td>
</tr>
<tr>
<td>V\text{appl}</td>
<td>Applied bias</td>
<td>-</td>
</tr>
<tr>
<td>\Omega\text{res}</td>
<td>Ohmic resistance</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>Photon matching</td>
<td>(yes)</td>
</tr>
<tr>
<td>\Delta\text{light, top}</td>
<td>Parasitic light absorption (top)</td>
<td>10%</td>
</tr>
<tr>
<td>\Delta\text{IPCE, top}</td>
<td>IPCE (top cell absorber)</td>
<td>100%</td>
</tr>
<tr>
<td>\Delta\text{light, bot}</td>
<td>Parasitic light absorption (bottom)</td>
<td>10%</td>
</tr>
<tr>
<td>\Delta\text{IPCE, bot}</td>
<td>IPCE (bottom cell absorber)</td>
<td>100%</td>
</tr>
<tr>
<td>M0</td>
<td>Dark saturation current (multiple)</td>
<td>100</td>
</tr>
<tr>
<td>R\text{sh}</td>
<td>Shunt resistance</td>
<td>10000 \Omega cm²</td>
</tr>
<tr>
<td>R\text{ser}</td>
<td>Series resistance</td>
<td>1</td>
</tr>
<tr>
<td>FE</td>
<td>Faradaic efficiency (HER)</td>
<td>100%</td>
</tr>
<tr>
<td>-</td>
<td>Thermodynamic potential</td>
<td>1090 mV (BrER)</td>
</tr>
<tr>
<td>-</td>
<td>1360 mV (ClER)</td>
<td></td>
</tr>
<tr>
<td>\Lambda</td>
<td>Ionic losses</td>
<td>1 M HBr (0.5cm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M HCl (0.5cm)</td>
</tr>
</tbody>
</table>

*While IPCE values usually consider light absorption by water film IPCE values here without water absorption are used as water absorption is considered separately.*

While the data presented in the main article were modelled to achieve a good comparison with existing literature data on PEC water splitting, in an actual device further parameters should be taken into consideration.

*Here a purely theoretical approach was used to calculate the optimal efficiencies in the different process. This purely theoretical approaches takes into account parasitic light absorption, otherwise it is assuming 100% photon-to-current conversion. For real devices,*
however, the light absorption is affected by the thickness/absorption coefficient of the sample. In case these properties are known they can be implemented in the WBM approach helping to improve the calculations.

Calculating efficiencies for these systems is not as straightforward as for systems where overall water splitting proceeds. For water splitting solar to hydrogen (STH) or solar to fuel values with the focus being only on hydrogen produced are reported. Thus, faradaic efficiency (FE) can quite easily be incorporated into the efficiency calculations. However, in this work products are formed at both the photoanode and –cathode and differences in FE might occur. Hence, at the photoanode a mixture of our desired product (Cl₂, Br₂, H₂O₂,) and the undesired product (O₂ evolution) are formed whereas the cathodic reaction proceeds with 100% FE. For the purposes of this paper, solar-to-chemical (STC) efficiencies are used instead. STC is defined in terms of the oxidation products given by equation S1.

\[ \text{STC}(E_g) = \frac{i \times E_{\text{Thermo}} \times F_{\text{eff, Oxidation}}}{P_{\text{input}}} \times 100\% \]  

For ClER and BrER it has been shown that in acidic solutions the production of oxygen is negligible and occur at 100% faradaic efficiency, which means STH and STC can be considered equivalent.[1–4] From a practical standpoint, there is the possibility for ppm levels of O₂ to be in the product stream.

The temperature was set to 298 K, i.e. room temperature, however, the actual device working temperature might exceed room temperature. Higher working temperatures might even increase efficiency of the devices by improving the kinetics of the reduction and oxidation reaction. Additionally an efficiency gain by cooling the products to room temperature can be expected.[5]

It should also be noted that losses associated with the ionic conductivity of a membrane are not yet considered in the model. With ionic conductivities of 243 mS/cm, 335
mS/cm and up to 200 mS/cm for 1 M HBr, 1 M HCl and Nafion membranes\cite{6}, respectively
the associated loss being rather small. Typically a membrane thickness of 200 µm is used and
thus a total ionic conductivity e.g. for 1 M HBr system of ≈230 mS/cm can be expected. For
processes in alkaline conditions were alkaline-anion exchange membranes are required the
ionic conductivities of these membranes are smaller and up to 20 mS/cm can be expected.\cite{7}
Considering the electrolyte conductivity of 1 M KOH (200 mS/cm) using a membrane of
similar thickness than Nafion this will result in ≈140 mS/cm. In both cases the drop in STC
efficiency would be less than 1%.

Finally it has to be noted that while parasitic light absorption has already been
considered there might be an additional parasitic light absorption associated with the
absorption by products, e.g. bromine and chlorine.\cite{8} This issue can easily been suppressed by
device design, e.g. in conventional designs oxidation is assumed to occur at the large band
gap top cell absorber.\cite{9} In this case light absorption by products might be an issue. By
switching the oxidation to the small band gap bottom cell light absorption by oxidation
products can easily been ruled out.

**Modelling data – Precision options**
**Determination of operating voltage an optimal efficiency point**

To determine the device voltage for a given combination of top cell/bottom cell band gaps, the efficiency at a given point was divided by the thermodynamic potential, which then gave the operating current of the device. By using the WBM sub-program that calculates i-V solar cells, the i-V curve of both the top cell and bottom cell photoabsorber could then be calculated (It is essential to make sure the water absorption, parasitic light absorption, etc. are all the same as in the solar fuels calculation). With both the operating current of the device known, as well as the i-V curves of each photoabsorber (top cell/bottom cell), the operating photovoltage is just a summation of the two voltages from the i-V curve at the operating current.

**Additional Figures**

![Figure S1](image)

**Figure S1.** Plot of STC efficiency for single band gap absorber for the baseline cases used to calculate the dual absorber devices, i.e. 100% FE.
Figure S2. Modelling results for HBr splitting using 1M HBr and no water film. Otherwise the parameters are as reported in Table 1 and Table S1. A maximum of STH 27.06% can be obtained with an optimal band gap combination of 1.52 eV/0.76 eV. This corresponds to a production rate of 4.69 mol/m²/hr.

Figure S3. Current matching by top cell absorber thinning is allowed to mitigate limitations by the bottom cell for HCl splitting. All other conditions were chosen as used for Figure 1 in the main text.
Figure S4. Changes in STH efficiency plots for varying electrolyte concentrations a) 0.01 M HBr, b) 0.1 M HBr and c) 0.01 M HCl. Otherwise the contour plots were calculated using the parameter set presented in Table 1 in the main article and Table S1. Maximum STH efficiencies of a) 12.07%, b) 19.65% and c) 13.64% corresponding to production rates of can be achieved with these conditions a) 2.07, b) 3.36 and c) 1.87 mol/m²/hr, respectively.
Figure S5. % thinning required for the top cell absorber to achieve the STH shown in Figure 2 d) for a photoelectrochemical device producing hydrogen and hydrogen peroxide. The data were calculated assuming a fixed overpotential of 150 mV and 1 M KOH as electrolyte.


