Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2021

Modeling and design guidelines of high-temperature

photoelectrochemical devices

Supplementary information

Ronald R. Gutierrez, Sophia Haussener

1 High-temperature solar cells vs. traditional pn-junction solar cells at high temperature

Two 1D models were developed to estimate the performance of i) traditional p-n junction solar cells and ii) high-temperature solar cells (HTSC) working with thermionic emission. Both models consider a n-doped layer ($N_D = 1e17 \text{ cm}^{-3}$ for traditional solar cells and $N_D = 1e16 \text{ cm}^{-3}$ for HTSCs) and a p-doped layer ($N_A = 1e18 \text{ cm}^{-3}$ for both cases). Temperature-dependent material properties and all the recombination mechanisms were considered. The performance is compared in figure S1 for working temperatures between 600 and 800 K. Note that the materials of the p- and n-doped semiconductors of the traditional junctions are the same, while the n-doped semiconductor of the HTSCs is GaP in all cases.



(a)

Fig. S1 I-V curves of different solar cells working at different temperatures (solid lines: 600 K, dashed: 700 K, dotted: 800 K) and at a solar concentration of 100 suns. Left side shows traditional p-n junction solar cells, right side shows high-temperature solar cells working with thermionic emission. The figure insets show the performance of the SiC solar cells. Note the materials the p-n junctions are the same while the material of the n semiconductor for the HTSCs is always GaP.

The results indicate better performance (in terms of open circuit voltage and short circuit current density) of HTSCs compared to traditional pn-junction solar cells when using GaAs and 4H-SiC. The latter, however, reach very low current densities due to poor solar light absorption. Figure S2 compares the solarto-electricity efficiency of both devices indicating better performing HTSCs when using GaAs, Si, and SiC materials.



Fig. S2 Solar-to-electricity as function of temperature for different solar cells. Left side: traditional p-n junction solar cells, right side: high-temperature solar cells working with thermionic emission.

2 Selective carrier extraction

The assembly allows to extract electrons at one side and holes at the other side thanks to the energy level difference in the conduction and valence bands. Increasing the voltage in the assembly increases the barrier that the electrons must overcome to reach the metal contact.



Fig. S3 Energy diagrams of the HTSC for a cell voltage lower and higher than the flat band.

3 High temperature solar cell model

The minority carrier concentration was determined by solving Poisson's equation, the transport and continuity equations for electrons and holes.

$$\nabla^2 \phi = -\frac{\mathrm{d}E}{\mathrm{d}y} = \frac{q}{\varepsilon} \left(n_{\mathrm{eq,e}} - n_{\mathrm{eq,h}} + N_{\mathrm{A}} - N_{\mathrm{D}} \right) \tag{S1a}$$

$$D_i \frac{\mathrm{d}^2 n_i}{\mathrm{d}y^2} \pm \mu_i \frac{\mathrm{d}(E \cdot n_i)}{\mathrm{d}y} = R(y) - G(y) = \frac{n_i}{\tau_i} - G(y) \tag{S1b}$$

$$\frac{1}{\tau_i} = \frac{1}{\tau_{\text{srh},i}} + \frac{1}{\tau_{\text{au},i}} + \frac{1}{\tau_{\text{rad},i}} = \frac{1}{\tau_{\text{srh},i}} + C_i \cdot n_{\text{eq},i}^2 + B \cdot n_{\text{eq},i}$$
(S1c)

Subscript *i* denotes electrons or holes, n_i is the minority carrier concentration, $n_{eq,i}$ is the minority carrier concentration at thermal equilibrium, D_i is the diffusion coefficient, μ_i is the minority carrier mobility (calculated with a temperature-dependent empirical model¹), *E* is the electric field computed with Poisson's equation (eq. (S1a)), and τ_i is the life time of the minority carrier. Equation (S1b) denotes that the balance between generation *G* and recombination *R* of carriers allows the transport of the minority carriers either by diffusion or by drift (positive sign for electron density).

The generation of photocarriers was computed assuming the photoabsorber as an absorbing, emitting, and non-scattering medium, for which we solved the radiative transfer equation:

$$\mu \frac{\mathrm{d}I_{\nu}(y,\mu)}{\mathrm{d}y} = \kappa_{\nu} \left(n_{\nu}^2 I_{\nu,b}[T(y)] - I_{\nu}(y,\mu) \right)$$
(S2)

where $I_{v,b}[T(y)]$ is the Planck function in vacuum, μ is the cosine of the polar angle of the direction, κ_v is the absorption coefficient, and n_v is the refractive index. The intensity boundary conditions to solve eq. (S2) follow the generalized form:

$$I_{\nu,j}(y,\mu_{\nu,j}) = (1 - \rho_{\nu,ij}(\mu_{\nu,i}))(n_{\nu,j}/n_{\nu,i})^2 I_{\nu,i}(y,\mu_{\nu,i}) + \rho_{\nu,ji} I_{\nu,j}(y,\mu_{\nu,j})$$
(S3)

where the subscripts *i* and *j* are used to indicate the upper and lower domain for the given boundary. For example, in the case of the upper boundary of the barrier (y = 0, see fig. 1a), *i* corresponds to the external environment and *j* corresponds to the barrier material. $\rho_{v,ij}(\mu_i)$ is the reflectivity of the interface for irradiation coming from domain *i* towards domain *j* with a cosine of the incidence polar angle μ_i . Note that at the extreme boundaries, the intensities coming from the external media, corresponds to the Plank function at the given temperature (ambient temperature at top boundary and anode chamber temperature at chamber boundary). Finally the generation G(y) was computed as follows:

$$G_{\nu}^{*}(y) = 2\pi \int_{-1}^{1} I_{\nu}(y,\mu) d\mu$$
(S4a)

$$G(y) = \int_0^\infty \frac{\kappa_v(y)G_v(y)}{hv} dv$$
(S4b)

The total photocurrent, eq. (S5a), is the sum of the electron and hole current at the interface between the barrier and the absorber, eq. (S5b). A positive sign is used for electrons.

$$i_{\rm sc}(y) = i_{\rm e}(y) + i_{\rm h}(y) \tag{S5a}$$

$$i_i(y) = q\mu_i n_i(y) E(y) \pm q D_i \frac{\mathrm{d}n_i(y)}{\mathrm{d}y}$$
(S5b)

4 Electrolyzer model

The operating voltage of the electrolyzer, V_e , is computed by solving the Butler-Volmer equation.

$$V_{\rm e} = E_{\rm O_2} - E_i + \eta_{\rm O_2} + \eta_i + \eta_{\rm ohm}$$
(S6a)

$$E_{\rm O_2} = E_{\rm O_2}^\circ - \frac{RT}{nF} \ln\left(\frac{1}{p_{\rm O_2, ref}}\right) \tag{S6b}$$

$$E_{i} = E_{i}^{\circ} - \frac{RT}{nF} \ln\left(\frac{p_{i,\text{ref}}}{p_{j,\text{ref}}}\right)$$
(S6c)

$$i_{i} = a_{v}i_{0,i} \left(\frac{p_{R}}{p_{R,ref}} \exp\left(\frac{\alpha_{a}nF\eta_{i}}{RT}\right) - \frac{p_{O}}{p_{O,ref}} \exp\left(\frac{-\alpha_{c}nF\eta_{i}}{RT}\right)\right)$$
(S6d)

$$i_{0,i} = k_i \exp\left(-\frac{E_{\text{act},i}}{RT}\right) \left(\frac{p_{\text{R}}}{p_{\text{R,ref}}}\right)^{-\alpha_c} \left(\frac{p_{\text{O}}}{p_{\text{O,ref}}}\right)^{-\alpha_a}$$
(S6e)

$$\sigma_{\rm a,c} = \frac{\sigma_{\rm a,c}^{\circ}}{T} \exp\left(-\frac{E_{\rm a,c}}{k_{\rm B}T}\right)$$
(S6f)

$$\sigma_{\text{elec}} = \sigma_{\text{elec}}^{\circ} \exp\left(-\frac{E_{\text{elec}}}{k_{\text{B}}T}\right)$$
(S6g)

The subscript *i* is used to denote the products of the reduction reactions (H₂ or CO), while *j* denotes the reactants (H₂O or CO₂). The equilibrium potentials are dependent on temperature and partial pressure, see eqs. (S6b) and (S6c). The partial pressures used in these equations are those at the inlet of the device, p_{ref} , to avoid numerical instabilities due to a possible division by zero at large current densities. The use of local partial pressures in the equilibrium potential was taken into account through the Butler-Volmer equation, eq. (S6d), and in the exchange current density, eq. (S6e), by adding the ratios p/p_{ref} (the subscript R is used to denote the reducing agent and O is used to denote the oxidizing agent). This allows to compute the same operating voltage as a model using local partial pressures but being able to stably compute solutions

at high current densities, where concentration overpotential start to dominate.

The pressure and velocity fields are determined by solving the Navier-Stokes and continuity equations in the fluid region, eqs. (S7a) and (S7b), while the Stokes-Brinkman and a continuity equations are solved in the porous region, eqs. (S7c) and (S7d). The combination of these equations is very convenient for problems where the flow velocity changes drastically from one region to another, i.e. high and low velocity in the free media, and porous media, respectively. The addition of mass to the flow due to the electrochemical reactions is taken into account by the mass source term, $Q_{\rm br}$. The effect of the porous electrode morphology on the pressure and velocity field is taken into account by the electrode porosity, $\varepsilon_{\rm p}$, and permeability, κ , in the Stokes-Brinkman equation. It is assumed that the velocity at the inlet is laminar, the velocity at the solid electrolyte-porous electrode interface is zero and there is not back-flow at the outlet of the chambers, see fig. 2a.

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot \left[-p\mathbf{I} + \mu \left(\nabla u + (\nabla u)^T \right) - \frac{2}{2}\mu (\nabla \cdot \mathbf{u})\mathbf{I} \right] + \mathbf{F}$$
(S7a)

$$\nabla \cdot (\rho \mathbf{u}) = 0 \tag{S7b}$$

$$\frac{\rho}{\varepsilon_{\rm p}} \left((\mathbf{u} \cdot \nabla) \frac{\mathbf{u}}{\varepsilon_{\rm p}} \right) = \nabla \cdot \left[-p\mathbf{I} + \mu \left(\nabla u + (\nabla u)^T \right) - \frac{2\mu}{3\varepsilon_{\rm p}} (\nabla \cdot \mathbf{u}) \mathbf{I} \right] - \left(\mu \kappa^{-1} + \beta_{\rm F} |\mathbf{u}| + \frac{Q_{\rm br}}{c^2} \right) \mathbf{u} + \mathbf{F}$$
(S7c)

$$\left(\begin{array}{c} \mu \mathbf{k} & + \rho_{\mathrm{F}} |\mathbf{u}| + \varepsilon_{\mathrm{p}}^{2} \end{array}\right)^{\mathbf{u}} + \mathbf{r}$$

$$\nabla \cdot (\rho \mathbf{u}) = Q_{\mathrm{br}} \tag{S7d}$$

The evolution of species along the anode and cathode channels is evaluated according to eq. (S8a). The first term on the left is related to the diffusive transport (Maxwell-Stefan diffusion model), the second term on the left corresponds to the convective transport, and the term on the right is related to the species sources, i.e. species generation and conversion by the electrochemical and thermochemical reactions (the signs in eq. (S8c) are positive for products).

$$\nabla \cdot \mathbf{j}_i + \rho(\mathbf{u} \cdot \nabla) \omega_i = R_i \tag{S8a}$$

$$\mathbf{j}_{i} = -\rho \,\omega_{i} \sum_{k} D_{ik} \left(\nabla x_{k} + \frac{1}{p_{\mathrm{A}}} \left((x_{k} - \omega_{k}) \nabla p_{\mathrm{A}} \right) \right) \tag{S8b}$$

$$R_i = \pm \frac{v_i i_v}{nF} \pm R_{\text{WGSR}} M_i \tag{S8c}$$

In the previous equations, ω_k , x_k , D_{ik} , p_A , and M_i , are referred to mass fraction, mole fraction, multicomponent Fick diffusivity, absolute pressure, and molar mass, respectively. The rate of water gas shift reaction can be determined by the following empirical equations^{2,3}:

$$R_{\rm WGSR} = k_{\rm sf} \left(p_{\rm H_2O} p_{\rm CO} - \frac{p_{\rm H_2} p_{\rm CO_2}}{K_{\rm ps}} \right) (\rm molm^{-3} \rm s^{-1})$$
(S9a)

$$k_{\rm sf} = 0.0171 \exp\left(-\frac{103191}{RT}\right) ({\rm molm}^{-3}{\rm Pa}^{-2}{\rm s}^{-1})$$
(S9b)

$$K_{\rm ps} = \exp\left(-0.2935Z^3 + 0.6351Z^2 + 4.1788Z + 0.3169\right)$$
(S9c)

$$Z = \frac{1000}{T(K)} - 1$$
 (S9d)

The temperature field is determined by the energy balance (S10a), where an effective thermal conductivity, k_{eff} , is used for the porous media. The effective conductivity is assumed to be a volume average of the bulk conductivity, weighted by the volume fraction, θ_{p} .

$$\rho C_{\rm p} \mathbf{u} \cdot \nabla T = \nabla \cdot (k_{\rm eff} \nabla T) + Q \tag{S10a}$$

$$k_{\rm eff} = \theta_{\rm p} k_{\rm p} + (1 - \theta_{\rm p}) k \tag{S10b}$$

The volumetric heat sources are added through the last term of the right side of eq. (S10a), Q, which is the sum of the Joule heating due to the charge transport in the solid conductors, eq. (S11b), and the heating due to electrochemical reactions, eq. (S11c). For the heat due to the electrochemical reaction, the first term represents the irreversible activation losses while the second part represents the reversible heat change due to the net change of entropy in the conversion process.

$$Q = Q_{\rm EC} + Q_{\rm JH} \tag{S11a}$$

$$Q_{\rm JH} = -(\mathbf{i}_{\rm s} \nabla \phi_{\rm s} + \mathbf{i}_{\rm l} \nabla \phi_{\rm l}) \tag{S11b}$$

$$Q_{\rm EC} = \sum_{i} \left(\eta_i + T \frac{\partial E_i}{\partial T} \right) i_i \tag{S11c}$$

5 Numerical methods and validation of the models

The HTSC model is a boundary-value problem of a second order differential equation. The equation was solved using the Matlab function bvp4c with an electron concentration tolerance of 1e-3 cm³. The tolerances allowed to satisfy the transport and continuity equation (eq. (S1b)) and the energy balance equation (eq. (4)). We used COMSOL Multiphysics 5.4 to solve the coupled multi-physics problem in the electrolyzer. Newton's method was used to solve the nonlinear systems at each node of the 2D model. The criteria of convergence was set to 1e-6 or a maximum number of 100 iterations, since further iterations didn't change the predicted voltage required by the electrolyzer, see figures S4a and S5a. A mesh conver-



(a)

Fig. S4 Operating voltage as function of a) the maximum number of iterations and b) the number of mesh elements for hydrogen generation at a current density of 10000 Am^{-2} . A mesh with 81080 elements was used to analyze the maximum number of iterations, while a maximum of 100 iterations was used for the analysis of the number of elements. The white markers indicate the selected mesh and maximum number of iterations.



Fig. S5 Operating voltage as function of a) the number of maximum iterations and b) the number of mesh elements for syngas generation at a current density of 10000 Am^{-2} . A mesh with 103100 elements was used to analyze the maximum number of iterations, while a maximum of 100 iterations was used for the analysis of the number of elements. The white markers indicate the selected mesh and maximum number of iterations.

gence analysis determined the number of elements to use, considering computational efforts and precision of the results. Figures S4b and S5b show the dependence of the operating voltage of the electrolyzer as function of the number of elements. Meshes with 81080 and 103100 triangular-quadrilateral elements were selected for the modeling of the electrolysis of water and concurrent water-carbon dioxide, respectively. This allows to compute the operating voltage of the electrolyzer with small relative errors of 0.74% (hydrogen formation) and 0.61% (syngas formation) with computational times of 10 min and 20 min, respectively.

5.1 Validation of the HTSC

We used the model presented by Yang et al.⁴ for the validation of our HTSC model. In their model they used a graded band-gap semiconductor $(Al_rGa_{1-r}As)$ in front of the absorber semiconductor. The generated carriers in the barrier are injected into the absorber (GaAs), and the emitted and reversed electrons crossed a vacuum layer before being collected by a metal electrode. Considering the same boundary conditions, and using the same materials, it was possible to compare our results with the results presented by their model. It can be noted in Fig. S6a that there is a good agreement between the current-potential curves (maximum difference of 1.30% in photocurrent density at 0 V, and root-mean-square difference of 0.474 Acm^{-2}). We obtained the same open circuit voltage but observed a small difference in the short current density (0.52 Acm^{-2}). We hypothesize that this difference is related to material properties used for the validation (e.g. absorption coefficient, bandgap, effective carrier mass, Richardson's coefficient) not given in Yang et al. Regarding the energy equations within the HTSC model to determine the heat sources and the HTSC temperature, eqs. (4) to (5), we validated our model by comparing our numerical results with those presented by Couderc et al.⁵ using a single-junction silicon solar cell. Fig. S7 shows a comparison between current-voltage, temperature-voltage, and power-voltage curves, our results under-predict the current density in 5.6%, the temperature in 4% at V = 0 V, probably due to the narrowing of the bandgap that was not considered in our model and thermal dependent optical properties. However, the trend of the curves and the range of values are acceptable considering that we didn't have access to all material parameters.



Fig. S6 (a) Current-voltage characteristics of heterostructured cathode with graded window-layer (Al_xGa_{1-x}As/GaAs cathode). Solar concentration C = 1000, cathode temperature $T_{\rm C} = 1000$ K, anode temperature $T_{\rm A} = 500$ K. (b) Comparison of the numerical and experimental results for high-temperature water, and concurrent water and carbon dioxide splitting.



Fig. S7 Comparison between the results from the current model and those achieved by Couderc et al.

5.2 Validation of the electrolyzer model

The electrolyzer model was validated with the experimental results of Momma et al.⁶ for water electrolysis, and Zhan et al.⁷ for co-electrolysis of water and carbon dioxide. The main parameters used in the model are shown in tables S1 and S2. The parameters not reported in Momma et al., namely electrode porosity and tortuosity, were extracted from Ni et al.⁸. The numerical results obtained by our model follow the trend of both experimental data (Fig. S6b), with coefficients of determination, R^2 , of 0.97 and 0.878 for the case of water and concurrent water-carbon dioxide splitting, respectively. In the case of water electrolysis, the operating potential was underestimated in the range of 2000 to 9000 Am⁻² and overestimated in the range of 10000-13000 Am^{-2} . This could be due to an inappropriate value for the charge transfer coefficient, which in our case was set constant and equal to 0.5, while in the experimental results it can be noted a change in the slope of the current-voltage curve, which was attributed by Momma et al. to an enlargement of the reaction site after a certain overvoltage⁶. Our model shows a slight change in the slope at high current densities, associated mainly due to the Joule heating effect in the electrodes and in the electrolyte and not due to a change in the morphology of the electrodes. With respect to the co-electrolysis of water and carbon dioxide, our numerical results underestimated the operating potential for current densities larger than 10000 Am^{-2} and showed earlier appearance of mass transport limitations. The voltage difference between the numerical and the experimental results was below 0.1 V for both cases and we hypothesize that this could be due to side reactions at the electrode. For instance in the case of the generation of syngas, the operating voltage starts to increase gradually after 10000 Am^{-2} , which could be due to degradation of the electrodes.

Table S1 Values used to compute the activation and ohmic overpotentials.

Parameter	Value	Material	
Activation energy, $E_{act,H_2}(Jmol^{-1})$	1.0e5 ^{2,9,10}		
Pre-exponential factor, $k_{\rm H_2}({\rm Am}^{-2})$	3.911e8 ^{2,11}		
Asymmetry factor, $\alpha_{\rm H_2}(-)$	0.5	Ni-YSZ	
Activation energy, $E_{\rm c}({\rm eV})$	0.099^{12}		
Pre-exponential factor, $\sigma_c^{\circ}(\text{SKm}^{-1})$	9.5e7 ¹²		
Specific surface area, $a_{\rm v,c}({\rm m}^{-1})$	1.025e5 ¹³		
Activation energy, $E_{act,O_2}(Jmol^{-1})$	1.2e5 ^{2,9,10}		
Pre-exponential factor, $k_{O_2}(Am^{-2})$	1.389e9 ^{2,11}		
Asymmetry factor, $\alpha_{O_2}(-)$	0.5	LSM-YSZ	
Activation energy, $E_{a}(eV)$	0.103^{12}		
Pre-exponential factor, $\sigma_a^{\circ}(\text{SKm}^{-1})$	4.2e7 ¹²		
Specific surface area, $a_{v,a}(m^{-1})$	1.025e5 ¹³		
Activation energy, $E_{\text{elec}}(\text{eV})$	0.887 ²	YSZ	
Pre-exponential factor, $\sigma_{elec}^{\circ}(Sm^{-1})$	33.4e3 ²		
Activation energy, $E_{\text{elec}}(\text{eV})$	0.60214	CGO	
Pre-exponential factor, $\sigma_{ m elec}^{\circ}(m Sm^{-1})$	$8.7 e4/T^{14}$		

Table S2 Values used to validate the electrolyzer model^{2,6-8} and for the reference case.

Parameter	Momma et al.	Zhan et al.	Present study	
Inlet temperature (K)	1273	1073	423	
Inlet velocity (m/s)	1.5	0.5	2	
Anode inlet gas molar ratio O ₂ /N ₂ (-)	0.21/0.79	0.21/0.79	0.21/0.79	
Cathode inlet gas molar ratio H ₂ /H ₂ O (-)	0.4/0.6	0.25/0.497	0.4/0.6 - 0.1/0.6	
Cathode inlet gas molar ratio CO/CO ₂ (-)	0/0	0.003/0.25	0/0 - 0.05/0.25	
Cathode chamber height (mm)	1	1	1	
Cathode thickness (μ m)	100	600	100	
Cathode porosity (-)	0.48^{8}	0.4	0.48	
Cathode tortuosity (-)	5.4 ⁸	2	5.4	
Electrolyte thickness (μ m)	1000	10	10	
Anode chamber height (mm)	1	1	2	
Anode thickness (μ m)	100	25	100	
Anode porosity (-)	0.48^{8}	0.3	0.48	
Anode tortuosity (-)	5.4 ⁸	2	5.4	
Chamber length (cm)	5	5	4	
Flow direction	Parallel flow	Parallel flow	Parallel flow	

6 Electrolyte material

The graph S8 shows a comparison of the ionic conductivity of different materials used as solid electrolytes. The graph also includes the ion conductivity of our ideal electrolyte that is based on the characteristics of Na_2CO_3 -SDC but with constant activation energy at different temperatures.

$$\sigma_{\text{elec}} = \frac{\sigma_{\text{elec}}^{\circ}}{T} \exp\left(-\frac{E_{\text{elec}}}{kT}\right)$$
(S12)

where we used a pre-exponential factor of $\sigma_{\text{elec}}^{\circ} = 1.3\text{e3} \text{ (Sm}^{-1}\text{K})$, an activation energy of $E_{\text{elec}} = 0.1088 \text{ eV}$).

7 Temperature and voltage gradients

Figure S9 compares the temperature evolution along the solid electrolyte and the local voltage for a device working in parallel and in counter-flow, the small air separation between the HTSC and the electrolyzer el-



Fig. S8 Ion conductivity as function of the temperature for different electrolytes.

ements allows a temperature difference which allows the HTSCs to work at lower temperature (Fig. S10a). The temperature rises very fast in the case of counter-flow, which could lead to unacceptable thermal stresses in the ceramic material of the electrodes and electrolyte (Fig. S10b).



Fig. S9 Temperature evolution along the solid electrolyte and voltage at the anode for the device working in (a) parallel flow, and (b) counterflow, at a solar irradiation concentration of 50 suns.



Fig. S10 a) Temperature distribution of the HTSC (solid lines) and the solid electrolyte (dotted lines) for the reference case. b) Thermal gradients in the solid electrolyte as function of the solar concentration for different scenarios.

8 I-V curves of the HTSCs and the SOE

The I-V curves of the solar cells and the electrolyzer for the reference case are shown in Fig. S11. The results show a change in the slope of the HTSC's I-V curves at high solar concentrations which is due to a rise of temperature.

9 Energy balance of the HTSC-electrolyzer

The energy balance in the solar cell and the overall system HTSC-electrolyzer verify that the incoming energy was conserved. In figure S12 the incoming solar radiation was converted into electrical power, but some parts were lost by reflection and heat losses, while the remaining energy was transmitted to the surface of the porous anode. In figure S13, the overall energy balance shows that part of the incoming solar radiation was converted into fuel, part was used to heat the reactants, part is lost by conduction at the inlets, while the rest is dissipated by convection and radiation to the external environment. Q_{error} shows the numerical error of the computation, the value is very small (below 0.25%) in all the studied scenarios.



Fig. S11 I-V curves of the HTSCs (solid lines) and the SOE (dashed lines) for a) the reference case at different solar concentrations and b) different scenarios at a solar concentrations of 50 suns.

10 Mean temperature of the HTSC ans SOE

Figure S14 shows how the mean temperature of the solar cell and the electrolyzer components change for each scenario and for different solar concentrations and the simulated solar concentrations.

11 Performance comparison of hydrogen and syngas

Figure S15 shows the improvement of molar flow rate of H_2 and efficiency of the device when producing syngas, both figures are with respect the reference case at 50 suns.



Fig. S12 Energy breakdown in the HTSC for different scenarios at a solar irradiation concentration of 50 suns.



Fig. S13 Energy breakdown in the HTSC-SOE device for different scenarios at a solar irradiation concentration of 50 suns.

12 Ideal photoabsorber

A parametric study of the material properties of the HTSC allowed to determine which properties showed most significant improvements in the performance at high temperatures. The most relevant parameters are the back surface velocity recombination, the electron SRH lifetime, and the radiative recombination coefficient, see figure S16.



(a)



(b)

Fig. S14 Temperature comparison for each scenario and solar concentration for the a) HTSC and b) the SOE.

13 Double junction solar cell

Higher photovoltages can be achieved by the use of double junction solar cells, in our case we added GaP/GaInP on top of GaP/GaAs and we evaluated its performance at different temperatures, see Fig. S17.



(a)



(b)

Fig. S15 a) Improvement of the molar flow rate of H_2 (%) for water splitting with respect to the reference case at 50 suns (8.24% STF efficiency and 17.37 mmolm⁻²s⁻¹). b) Improvement of the STF efficiency (%) for the generation of syngas (8.34% STF efficiency with molar flow rates of 16.2 mmolm⁻²s⁻¹ and 1.34 mmolm⁻²s⁻¹ for H_2 and CO, respectively).

14 Syngas generation

The energetic efficiency for most scenarios is quite similar to the reference case, only significant improvements are achieved if the number of HTSCs is reduced or by using a HTSC with better performance. On the



Fig. S16 I-V curves of the HTSC for different material properties at a solar irradiation concentration of 100 suns and temperatures of 600 K (red), 700 K (orange), and 800 K (yellow). Curves with varying a) front surface velocity recombination, b) back surface velocity recombination, c) electron Shockley-Read-Hall life time, d) Auger recombination coefficient, e) radiative recombination coefficient, and f) ideal case are shown.

other hand, the generation of syngas in a ratio of $H_2/CO = 2$, can only be achieved if more CO is produced. This was mainly achieved by reducing the amount of water and increasing the amount of CO_2 at the inlet of the device.



Fig. S17 Comparison of single and double junction HTSCs. The single junction is composed of GaP/GaAs while the double junction is composed of GaP/GaInP-GaP/GaAs. Both solar cells work at 600 K (solid lines), 700 K (dashed lines), and 800 K (dotted lines) and a solar concentration of 100 suns.



Fig. S18 a) STF efficiency, and b) molar flow rate of H₂ and CO (inset) for different scenarios as function of solar concentration.



(a)

Fig. S19 H₂O and CO₂ conversion for different scenarios when a) generating only H₂, and b) syngas as function of solar concentration.

15 Conversion of H₂O and CO₂

The conversion was computed according to the following expression:

$$X_i = \frac{\dot{n}_{i,\text{out}} - \dot{n}_{i,\text{in}}}{\dot{n}_{i,\text{in}}}$$
(S13)

Where $i = H_2O$, CO_2 , and \dot{n} is the molar flow rate.

16 Water gas shift reaction

Due to the partial pressures of H_2O and CO_2 , it is possible to improve the generation of CO by the thermochemical reaction at the porous cathode. Only in the scenarios where the inlet molar fraction of water was reduced and at the same time the inlet molar fraction of CO_2 was increased, CO was generated for all solar concentrations. In other scenarios, we observed mostly a consumption of CO in order to produce H_2 .



Fig. S20 Generation and consumption of H₂ (dashed lines) and CO (solid line) by the thermochemical reaction in the porous cathode.

List of Symbols

Charge transfer coefficient α Permittivity ε $\varepsilon_{\rm p}$ Porosity Ohmic overpotential $\eta_{
m ohm}$ Activation overpotential η_i Spectral absorption coefficient κ_V Cosine of the polar angle of the direcμ tion/Viscosity Mobility of electrons and holes μ_i Mass fraction ω φ Electrostatic potential Electric/Ionic potential $\phi_{s/l}$ Density ρ Spectral reflectivity ρ_v σ° Pre-exponential factor Shockley-Read-Hall recombination lifetime $au_{
m srh}$ Specific surface area $a_{\rm v}$ Radiative recombination В $C_{\rm e/h}$ Auger recombination $C_{\rm p}$ Specific heat constant Diffusion coefficient D Multi-component Fick diffusivity D_{ik} Ε Electric field Eact Activation energy Fermi level of electrons/holes $E_{\rm F}$ Half equilibrium potential E_i F Faraday's constant G(y)Local generation rate i_0 Exchange current density

	$I_{v,b}$	Spectral Planck function		
	I_V	Spectral radiation intensity		
	$i_{s/l}$	Electric/Ionic current density		
	k	Conductivity of fluid media		
	k _{eff}	Effective conductivity		
	<i>k</i> _p	Conductivity of porous media		
	<i>k</i> _i	Pre-exponential factor		
	М	Molar mass		
	n	Number of electrons		
	n_V	Spectral refractive index		
	$N_{\rm A/D}$	Acceptor/Donor concentration		
	$n_{\rm e/h}$	Photo-excited electron/hole concentration		
	<i>n</i> _{eq,e}	Electron/Hole concentration at equilibrium		
	р	Partial pressure		
	p_{A}	Absolute pressure		
	q	Elementary charge constant		
	$Q_{ m EC}$	Electrochemical heat source at the electrodes		
	$Q_{ m JH}$	Heat source by Joule effect in the elec-		
		trolyzer elements.		
	R	Ideal gas constant		
	R(y)	Local recombination rate		
$R_{\rm WGSR}$ Rate of water gas shift reaction				
	и	Velocity		
	$V_{\rm A}$	Relative work function of the electrode		
	V _C	Relative work function of the absorber		
	Ve	Electrolyzer voltage		
	V_{fb}	Flat band potential		
	$V_{\rm sc}$	Photovoltage		
	X_i	Molar conversion		
	x _i	Molar fraction		
	у	Spatial coordinates		

References

- 1 M. Sotoodeh, A. H. Khalid and A. A. Rezazadeh, J. Appl. Phys., 2000, 87, 2890–2900.
- 2 M. Ni, Journal of Power Sources, 2012, 202, 209-216.
- 3 B. A. Haberman and J. B. Young, International Journal of Heat and Mass Transfer, 2004, 47, 3617–3629.
- 4 Y. Yang, W. Yang and C. Sun, Sol. Energy Mater. Sol. Cells, 2015, 132, 410–417.
- 5 M. A. Romain Couderc and M. Lemiti, IEEE J Photovoltaics, 2016, 6, 1123–1131.
- 6 A. Momma, T. Kato, Y. Kaga and S. Nagata, J. Ceram. Soc. Jpn., 1997, 105, 369–373.
- 7 Z. Zhan, W. Kobsiriphat, J. R. Wilson, M. Pillai, I. Kim and S. A. Barnett, Energy & Fuels, 2009, 23, 3089–3096.
- 8 M. Ni, M. Leung and D. Leung, International Journal of Hydrogen Energy, 2007, 32, 2305–2313.
- 9 E. Hernandez-Pacheco, M. D. Mann, P. N. Hutton, D. Singh and K. E. Martin, Int. J. Hydrogen Energy, 2005, 30, 1221–1233.
- 10 P. Costamagna and K. Honegger, J. Electrochem. Soc., 1998, 145, 3995-4007.
- 11 S. H. Chan and Z. T. Xia, J. Appl. Electrochem., 2002, 32, 339–347.
- 12 M. Andersson, J. Yuan and B. Sunden, Journal of Power Sources, 2013, 232, 42,54.
- 13 V. Menon, Q. Fu, V. M. Janardhanan and O. Deutschmann, J. Power Sources, 2015, 274, 768-781.
- 14 P. Huang and A. Petric, J. Electrochem. Soc., 1996, 143, 1644–1648.