Electronic Supplementary Information

Exploiting Heat Transfer to Achieve Efficient Photoelectrochemical CO₂ Reduction

under Light Concentration

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Positioning of the photoelectrochemical (PEC) cell behind the Fresnel lens for light concentration tests

As shown in **Fig. S1**a, parallel light at an intensity of 1 sun hits the Fresnel lens and is then concentrated in the form of a cone with a maximum concentration factor at the focal length $(l_{\rm F} = 5.1 \text{ cm})$ of the lens. The light intensity behind the lens depends on the distance (*h*) from the lens and on the illuminated area (*A*₂) of the lens. The concentration factor (*c*) can be determined by the ratio of *A*₂ and the area of the circular conic section (*A*₁) at a given distance *h*:

$$c = t \frac{A_2}{A_1} = t \frac{r_2^2}{r_1^2},\tag{1}$$

using the transmission of the lens (*t*) and the radii (r_1 , r_2) of the circles A_1 and A_2 . For our calculations, we assumed a uniform *t* of 90%, according to the wavelengths of interest on the Thorlabs datasheet.¹ Using the intercept theorem on the conical frustum encompassed by A_1 and A_2 leads to:

$$h = l_{\rm F} \left(1 - \frac{r_1}{r_2} \right) \tag{2}$$

and therefore:

$$c = \frac{t}{\left(1 - \frac{h}{l_{\rm F}}\right)^2}.$$
(3)

Fig. S1b shows the calculated *c* as a function of *h*. Good agreement is achieved with measured values. The dashed rectangles in **Fig. S1**b mark the boundaries for uniform illumination based on the size of the solar cell illuminated by the concentrated sunlight. If the distance between the solar cell and the lens surpasses those limits, the corners of the photovoltaic (PV) will no longer be illuminated.



Fig. S1. Positioning of the PEC cell behind the Fresnel lens. (a) Illustration of the basic geometry present in Fresnel lens applications. We note that using circular Fresnel lenses and rectangular solar cells will always lead to lost illumination areas due to the shape mismatch, unless the solar cells are illuminated nonuniformly, leaving its corners in the dark. However, the lost illumination area may still be used to heat up surrounding electrocatalytic surface, potentially enhancing reaction kinetics.² (b) Concentration factor as a function of the distance between Fresnel lens and illuminated object. The dashed rectangles mark the boundaries for uniform illumination of square solar cells with side lengths (*a*) of 1 and 2 cm.



Fig. S2. Illustration of the critical voltage (V_{crit}) using exemplary cyclic voltammetry (CV) curves for PV and electrochemical (EC) components. To avoid current losses larger than 0.2% of the PV short circuit current (I_{sc}), the current of the EC component should be larger than I_{sc} at V_{crit} . At the same time, V_{crit} needs to be slightly smaller than the voltage at the maximum power point (MPP) of the PV and marks the point where the PV polarization curve transitions from a flat line to an exponentially decreasing curve.



Fig. S3. CV comparison between Ni- and Ir-coated anodes indicating similar performance. For both tests, the anode was fed with 1M potassium hydroxide at a flow rate of 0.05 mL min⁻¹ using a syringe pump. The cathodes consisted of gold catalysts were sputtered on Toray carbon paper without micro-porous layer (MPL). During the measurement, 10 sccm humidified carbon dioxide was fed into the cathode chamber.



Fig. S4. Performance comparison between Toray- and AvCarb-supported Au cathodes. For both tests, Ni served as the anode catalyst. A syringe pump was used to push 1 M KOH through the anode chamber at a flow rate of 0.05 mL min⁻¹, while 10 sccm humidified CO₂ was flowed through the cathode chamber. (a) CV comparison showing a slightly improved performance of the AvCarb-supported (with MPL) Au cathode. (b) Stability test of the AvCarb-supported Au cathode at 2 V applied bias. (c) One-hour test of the AvCarb-supported Au cathode at 3 V applied bias, indicating unstable performance at this voltage. However, with a desired operating voltage below V_{crit} (~2.1 V), this is less problematic. This test also showed cumulative faradaic efficiencies significantly below 1 due to measurement errors of the comparatively high carbon monoxide concentrations in the cathode outlet. These

measurement errors can be reduced by diluting the cathode outlet with an inert gas such as argon, forcing the CO concentrations in the outlet towards the calibration limits of the gas chromatograph (GC) detectors (see Experimental Section in the main manuscript).



Fig. S5. Variation of the analyte concentration from 1 M to 5 M KOH at a flow rate of 0.05 mL min⁻¹. As indicated by the CVs in (a) and CAs at 2 V in (b), the performance continuously increases from 1 M to 5 M. For all measurements, 10 sccm humidified CO₂ was fed into the cathode chamber.



Fig. S6. Variation of the 1M KOH anolyte flow rate using a peristaltic pump. Higher flow rates increase the current at 2 V applied bias but also increase CO₂ crossover through the membrane (**Fig. S7**). CO₂ utilization efficiencies were around 3% during these experiments and were not impacted by the variation of flow rates and increased CO₂ crossover. However, CO₂ crossover may ultimately limit CO₂ utilization efficiencies under conditions of low CO₂ availability.^{3,4} For all measurements shown here, 10 sccm humidified CO₂ was fed into the cathode chamber. (a) Full range of measured currents. (b) Zoomed-in range of measured currents to highlight the final, stabilized currents.



Fig. S7. Performance decrease caused by acidification of the anolyte via CO_2 crossover through the membrane. For all results shown here, 10 sccm humidified CO_2 was fed into the cathode chamber. (a) The current quickly decreases at 2 V applied bias while the cathode outlet flow rate increases over the course of one hour. As more CO_2 crosses from the cathode to the anode, the anolyte slowly saturates with CO_2 , increasing the solvent pH and slowing down subsequent CO_2 crossover. Within 5 h of operation, a pH change from ~14 to ~11 was observed. During this measurement, 15 mL of 1M KOH anolyte was circulated through the anode at 3.6 mL min⁻¹. Spikes in the cathode outlet flow rate were caused by GC injection and ejection valve switches. (b) CV comparison between acidified (old) KOH and fresh KOH shows a clear increase of the onset potential with old KOH. The CV with fresh KOH was

measured with the same device, only the KOH electrolyte was exchanged. In both cases, 1M KOH anolyte was circulated through the anode at 3.6 mL min⁻¹. (c) When a more acidic 1M KHCO₃ anolyte is used instead of 1M KOH, the CV appears similar to the acidified KOH case. A syringe pump was used to push the electrolyte through the anode at 0.05 mL min⁻¹ for both CVs shown. (d) The current degradation rate increases with the KOH flow rate. Currents measured during the last 3 hours of 6 h stability tests at 2 V applied bias were used to calculate the degradation rates. For all flow rates tested, 15 mL of 1M KOH anolyte was circulated through the anode.



Fig. S8. PV CVs at different light intensities measured near room temperature, just after opening the shutter of the solar simulator and without electrolyte in the PEC cell. The short circuit currents measured at the different light intensities match well when normalized by the light intensity, indicating accurate positioning of the Fresnel lens and photoabsorber. The illuminated area of the PV was 0.94 cm^2 . J_{sc} represents the short circuit current density, V_{oc} the open circuit voltage, J_{MPP} and V_{MPP} the current density and voltage at the maximum power point, respectively.



Fig. S9. Equilibration experiment conducted over ~ 1 h at 2 V applied bias and without illumination of the PEC device. During the equilibration, KOH anolyte slowly wets the membrane and subsequently the cathodic catalyst surface, increasing the electrochemically active surface area (ECSA) by a factor of ~ 10 . The ECSA was calculated by estimating the double layer capacitance of the catalyst surface (via measurements of CVs at different scan rates in a non-faradaic region).^{5,6}



Fig. S10. Operation of the PEC device at 1 sun illumination intensity without external bias.(a) After a short equilibration time, the voltage and current were stable during the 1 h test.

(b) The cumulative faradaic efficiencies were near unity. (c) The product distribution shows a high selectivity for CO, with CO/H_2 ratios near 30:1. (d) CVs of the PV taken before and after the 1 h test indicate excellent stability. (e) The stability is further evidenced by PEC CVs taken before and after the 1 h stability test with no performance degradation observed.



Fig. S11. Operation of the PEC device at 3.02 suns illumination intensity without external bias. (a) Voltage and current were stable during the 1 h test. (b) The cumulative faradaic efficiencies were near unity. (c) The product distribution shows a high selectivity for CO, with CO/H_2 ratios near 30:1. The CO_2 utilization efficiency was enhanced compared to the test at 1 sun (**Fig. S10**) due to the higher current from light concentration. (d) CVs of the PEC device taken before and after the 1 h test indicate excellent stability.



Fig. S12. Operation of the PEC device at 5.05 suns illumination intensity without external bias. (a) CVs of the PV taken before and after the 17 h test indicate excellent stability. The fill factor drop is caused by a slow increase in PV temperature during operation. (b) The

stability is further evidenced by CVs in full PEC mode. (c) The cumulative faradaic efficiencies were slightly above 1 (maximum: 1.03), most likely due to inaccuracies of the flow meter placed at the cathode outlet. For solar conversion efficiency calculations, all faradaic efficiency values were scaled proportionally (maximum adjustment factor: 1.03) to yield a maximum, cumulative faradaic efficiency of 1. (d) The CO/H₂ ratio fluctuated from 20:1 to 10:1 with CO₂ utilization efficiencies near 1%. (e) An energy efficiency between 51-65% was achieved throughout the stability test (see Experimental Section in the main manuscript).



Fig. S13. EC stability test at an applied bias of 2.15 V without illumination to demonstrate bubble trapping. Three extra layers of carbon paper were used in the anode chamber and the remaining operating conditions were kept the same as during the PEC test shown in **Fig. 3** of the main manuscript. Specifically, 60 sccm of humidified CO_2 was flowed through the cathode chamber and 2M KOH was circulated through the anode chamber at 5.9 mL min⁻¹. (a) The measured current as a function of time shows fluctuations that are similar to those seen during the PEC test (**Fig. 3**). The highlighted time period indicates the imaging time shown in the Supporting Video, taken from the anode side of the device. (b) Current as a function of time for one specific current spike. The Supporting Video is played at 200x speed until the current starts to rise, after which it is played at 1x speed. At 1x speed, the video clearly shows significant bubble evolution in the anode chamber as the current starts to increase. When trapped O₂ bubbles are released from the anodic catalyst layer, more catalytic sites become available, resulting in the rapid current increase.



Fig. S14. Product ratio as a function of the measured voltage and current. High CO/H_2 ratios can be maintained at low voltages combined with high currents or high voltages combined with low currents.



Fig. S15. Variation of the CO₂ flow rate at an applied bias of 2.15 V without illumination to achieve higher CO₂ utilization efficiencies. (a) The equilibrated current after 2 h of operation is only slightly lower at 1 sccm CO₂ flow rate compared to 60 sccm. However, the device is more sensitive to short pressure fluctuations caused by GC injection and ejection valves when using low CO₂ flow rates. (b) The CO₂ utilization efficiency increases by a factor of 20 with the reduced CO₂ flow rate of 1 sccm. For the experiments with lower flow rates of 1 and 10 sccm CO₂, the cathode outlet was diluted with Ar to stay within the CO calibration limits of the GC (see Experimental Section in the main manuscript).



Fig. S16. Dilution of the cathodic CO₂ inlet with N₂ to achieve higher CO₂ utilization efficiencies. A syringe pump was used to pump 1M KOH through the anode at 0.05 mL min⁻¹ and the total cathodic flow rate was kept at 10 sccm. (a) Reducing the CO₂ concentration in the cathode inlet stream leads to an enhanced CO₂ utilization efficiency with minor increases in the H₂/CO product ratio until 5% CO₂ content. Further reductions only lead to significantly increased H₂ evolution. (b) Both the onset potential and peak currents are increased when the product ratio is skewed towards H₂, consistent with our previous results.⁷



Fig. S17. Current fluctuation analysis. (a) Operating point over 17 h of operation, plotted together with the full-scale EC and PV curves. The PV short circuit current measured at the beginning of operation was 58.1 mA. (b) Percentage of available EC area during the 17 h test compared to the reference curve shown in (a). (c) Percentage of PV losses contributing to the total losses. During most of the time during the experiment, PV losses contribute less than 10% to the total loss. Fluctuations occur when the total current losses are very small due to low operating voltages, causing the PV curves measured before and after operation to converge and making an accurate assignment of losses more difficult.



Fig. S18. PV temperature in the reference cell assembly at 5 suns illumination intensity. The temperature of the uncooled PV increases quickly after the shutter of the light source is opened (t = 0). As the temperature increases, the fill factor of the PV drops. We note that the PV temperature is expected to rise much slower in the full PEC assembly due to the higher heat capacity of the liquid-filled PEC cell. Similarly, the final PV temperature is anticipated to be lower due to convective cooling by liquid electrolyte. However, a similar correlation between PV temperature and fill factor can be expected in the PEC cell.



Fig. S19. PV efficiency gains via electrolyte cooling. (a) PV and electrolyte temperatures as a function of the light intensity in the PIM assembly. The analyte temperature was measured directly at the anode outlet (red data points), which can be assumed to be roughly equal to the temperature of the anode in the cell,² and in the liquid reservoir (blue data points). Upon illumination, the electrolyte temperature increases. The light intensity does not have a significant effect on the electrolyte temperature, since the amount of photons hitting the device (PV plus EC area) remains essentially constant. At 1 sun, the whole cell is illuminated, while at 5 suns the light is focused on the PV portion of the cell. If photons are hitting only the PV portion at 1 sun, the electrolyte temperature decreases by ~1 °C compared to full cell illumination. The analyte temperature at the anode outlet equilibrates within 15 minutes, while the temperature in the reservoir responds slower due to the comparatively large volume (~200 mL). The PV temperature was measured while flowing DI water at 5.9 mL min⁻¹ instead of KOH to prevent corrosion of the thermocouple attached to the PV back surface. The PV temperature is significantly cooler across all tested light intensities when flowing liquid over the PV back surface compared to the dry case. Error bars indicate the standard deviation of the temperature during the last 10 min of the measurement. (b) Absolute PV efficiency gains due to cell cooling.



Fig. S20. Beneficial cooling during PEC operation quantified with respect to the PV curve measured after 17 hours of operation. (a) PV gains calculated as the current difference between operating point and final PV curve (see **Fig. 4**). (b) Fraction of the total solar conversion efficiency enabled by cooler PV temperatures compared to the final PV temperature after operation. These values were calculated via dividing the PV current gains by the total measured current during operation.



Fig. S21. Beneficial cooling during PEC operation calculated with respect to an uncooled PV curve at 5 suns illumination intensity. (a) Comparison of the operating point with EC and PV CVs. The operating point lies between the uncooled reference PV curve at equilibrium temperature and the PV curve before operation near room temperature. (b) PV gains calculated as the current difference between operating point and uncooled reference PV curve (see **Fig. 4**).



(a)





(c)

(d)

Fig. S22. Surface analysis after 17 h of operation. (a) Energy dispersive X-ray spectroscopy (EDS) image of the anodic, Ni-coated carbon paper showing uniform catalyst coating after operation. (b) EDS image of the cathodic, Au-coated MPL on carbon paper after operation. Due to catalyst delamination, Au can only be detected on parts of the carbon paper. (c) High magnification EDS image of the cathodic, Au-coated MPL on carbon paper. Traces of KOH crystals can be detected as a result of anolyte crossover through the membrane. (d) Optical microscope image showing Au adhesion to the membrane after operation.

References

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