

# Hydrogen production with a microbial biocathode

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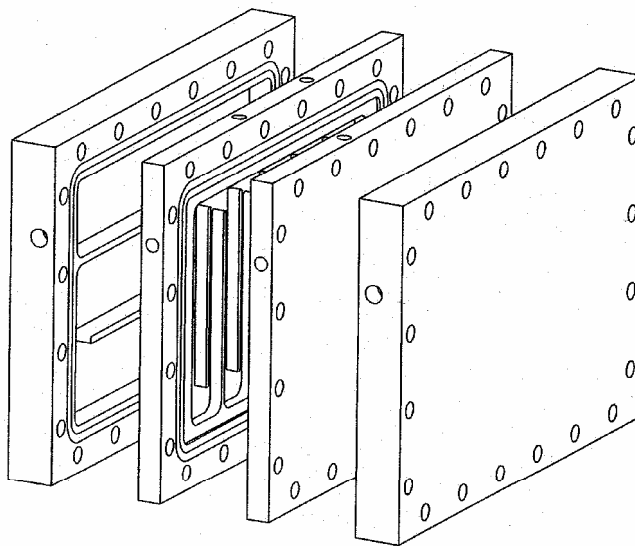
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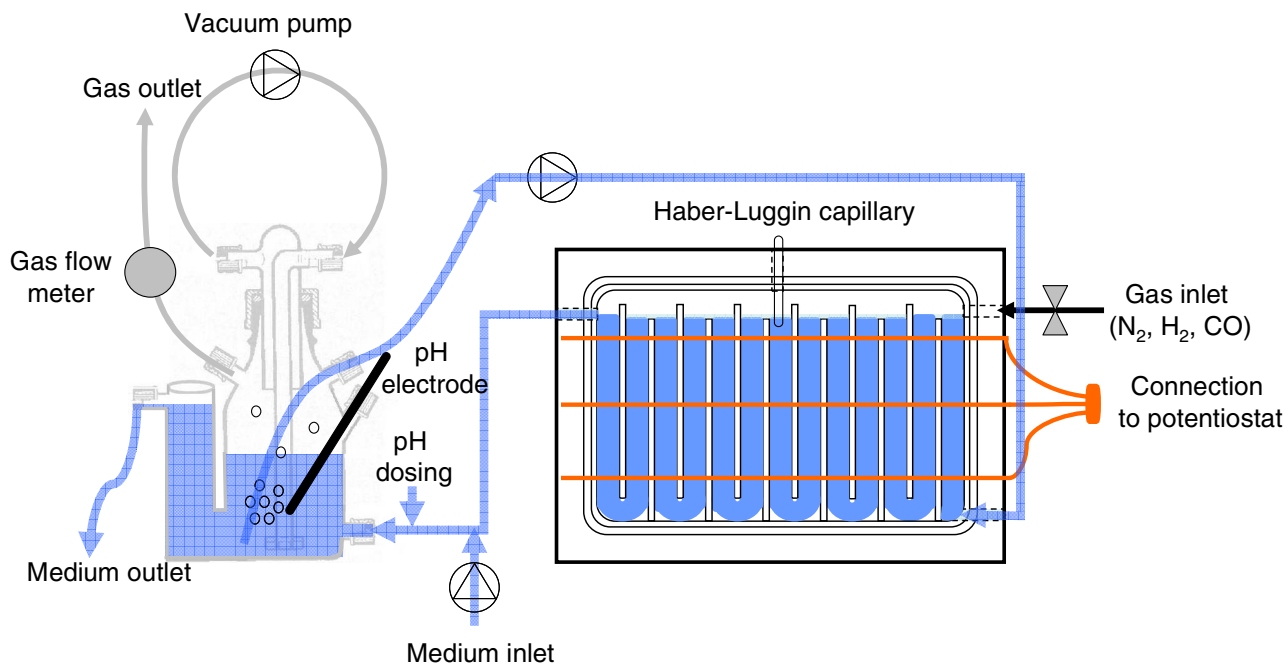
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**Supporting Information:** [5](#) pages, [5](#) figures, [1](#) table



**FIGURE S1.** Design of the Plexiglas plates (22 x 32 cm) of the electrochemical cells. The two outer plates served as the heating jacket for temperature control; the two inner plates served as the electrode chambers and were separated from each other by a cation selective membrane (Fumasep® FKE, FuMA-Tech GmbH, Germany).



**FIGURE S2.** Schematic overview of the experimental set-up.

## Calculation of the diffusional hydrogen loss through the membrane during the hydrogen yield tests:

As previously shown by Liu and Logan (1), the rate of diffusion of a gas through a membrane in a bioelectrochemical cell can be conveniently estimated according to:

$$W = -DA \frac{dC}{dx} \cong -DA \frac{\Delta C}{\delta_m} \quad (1)$$

with  $W$  the rate of diffusion of a gas (in mol/s),  $D$  the diffusion coefficient of the gas in the membrane (in  $\text{cm}^2/\text{s}$ ),  $A$  the cross-sectional area of the membrane ( $280 \text{ cm}^2$ ),  $\Delta C$  the hydrogen concentration difference between both sides of the membrane (in  $\text{mol}/\text{cm}^3$ ), and  $\delta_m$  the thickness of the membrane ( $0.006 \text{ cm}$  for Fumasep<sup>®</sup> FKE). To estimate the hydrogen diffusion through the Fumasep<sup>®</sup> FKE membrane, we assumed no hydrogen at the anode side of the membrane and hydrogen saturation at the cathode side of the membrane at the average hydrogen headspace concentration during the hydrogen yield tests of about 28.5%. Further, we assumed in our calculation that the hydrogen diffusion characteristics in the Fumasep<sup>®</sup> FKE membrane were similar to those in Nafion<sup>®</sup> as determined by Jiang and Kucernak (2). Jiang and Kucernak determined the hydrogen diffusion coefficient ( $D$ ) and solubility of hydrogen ( $c^0$ ) in Nafion<sup>®</sup> at 293 and 313 K. The diffusional hydrogen loss at 303 K is expected to be in between the calculated values at 293 and 313 K:

Table S1. Calculation of the diffusional hydrogen loss through the Fumasep<sup>®</sup> FKE membrane during the 48 hour of the hydrogen yield tests at 303 K.

T (K)	$D$ ( $\text{cm}^2/\text{s}$ )	$c^0$ ( $\text{mol}/\text{cm}^3$ )	$W$ ( $\text{mol}/\text{s}$ )	$W$ (at 303 K) (L/48 h)
293	$7.6 \times 10^{-6}$ <sup>a</sup>	$5.1 \times 10^{-7}$ <sup>a</sup>	$5.2 \times 10^{-8}$ <sup>b</sup>	<b>0.22</b>
313	$1.29 \times 10^{-5}$ <sup>a</sup>	$4.2 \times 10^{-7}$ <sup>a</sup>	$7.2 \times 10^{-8}$ <sup>b</sup>	<b>0.31</b>

a. Hydrogen diffusion coefficient ( $D$ ) and solubility of hydrogen ( $c^0$ ) at 293 and 313 K from Jiang and Kucernak (2).

b. At an average hydrogen headspace concentration of 28.5%  $\rightarrow \Delta C = 28.5/100 \times c^0$ .

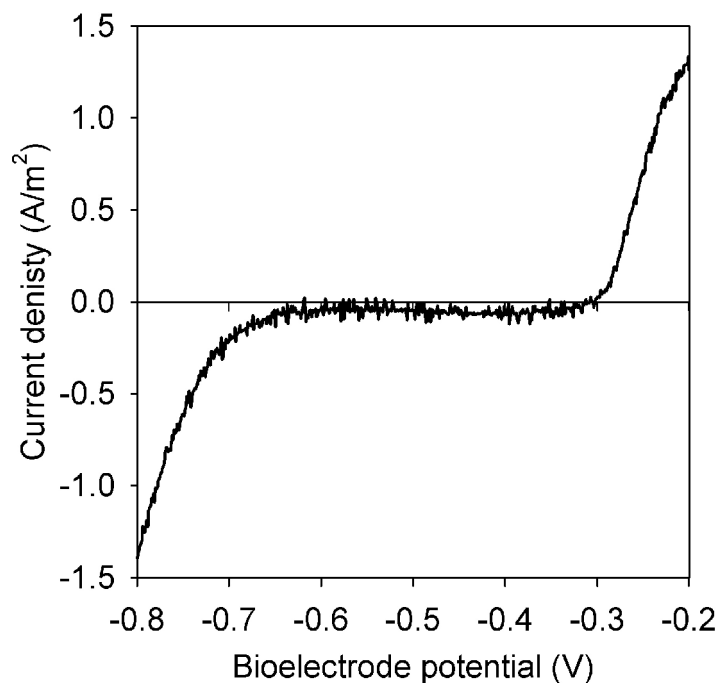


FIGURE S3. Polarity reversal scan of the bioelectrode from -0.2 to -0.8 V at a scanrate of 0.025 mV/s.

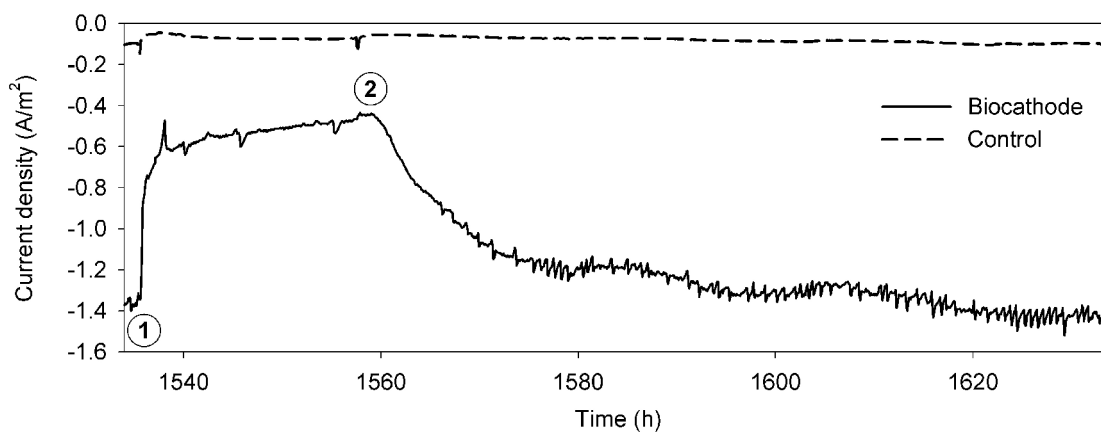
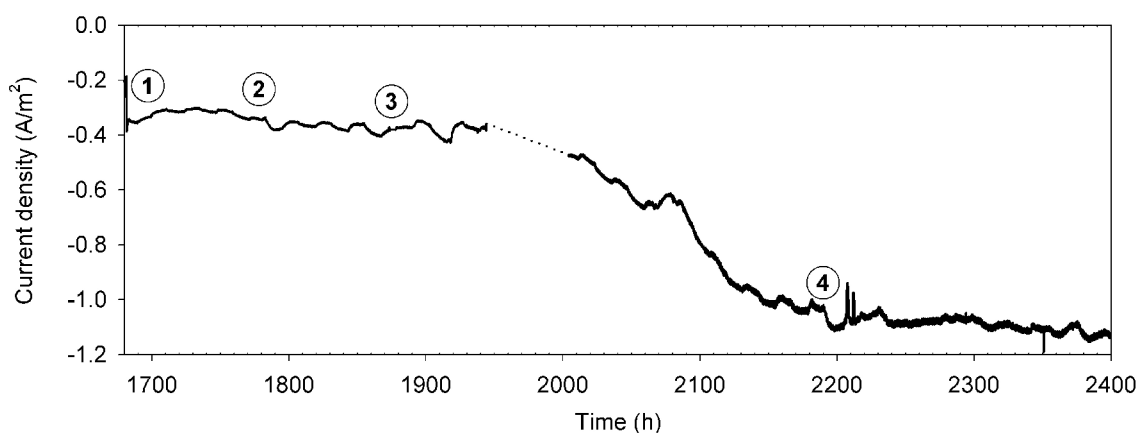


FIGURE S4. Current development of the biocathode and the control electrode in response to carbon monoxide flushing: (1) start of carbon monoxide flushing of the headspace of the biocathode chamber and the control electrode chamber, and (2) end of carbon monoxide flushing and start of nitrogen flushing of the headspace of the biocathode chamber and the control electrode chamber.



**FIGURE S5. Cathodic** current development of the control electrode after inoculation (dotted line = no data due to power cut): (1) inoculation of the control electrode chamber by connecting the medium outlet of the biocathode chamber to the medium inlet of the control electrode chamber, (2) disconnection of the medium outlet of the biocathode chamber from the medium inlet of the control electrode chamber and start of the supply of standard microbial nutrient medium (i.e without carbon source), (3) start of the supply of standard microbial nutrient medium supplemented with 10 mM sodium bicarbonate, and (4) start of the supply of standard microbial nutrient medium (i.e without carbon source).

### Literature Cited

- (1) Liu, H.; Logan, B. E. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ. Sci. Technol.* **2004**, *38*, 4040-4046.
- (2) Jiang, J. H.; Kucernak, A. Investigations of fuel cell reactions at the composite microelectrodesolid polymer electrolyte interface. I. Hydrogen oxidation at the nanostructured Pt/Nafion<sup>®</sup> membrane interface. *J. Electroanal. Chem.* **2004**, *567*, 123-137.