Significance of Biological H_2 Oxidation in a Continuous Single-Chamber Microbial Electrolysis Cell

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7 figures, 1 table, and 11 pages

1. A Schematic Diagram of the Upflow Single-Chamber MEC

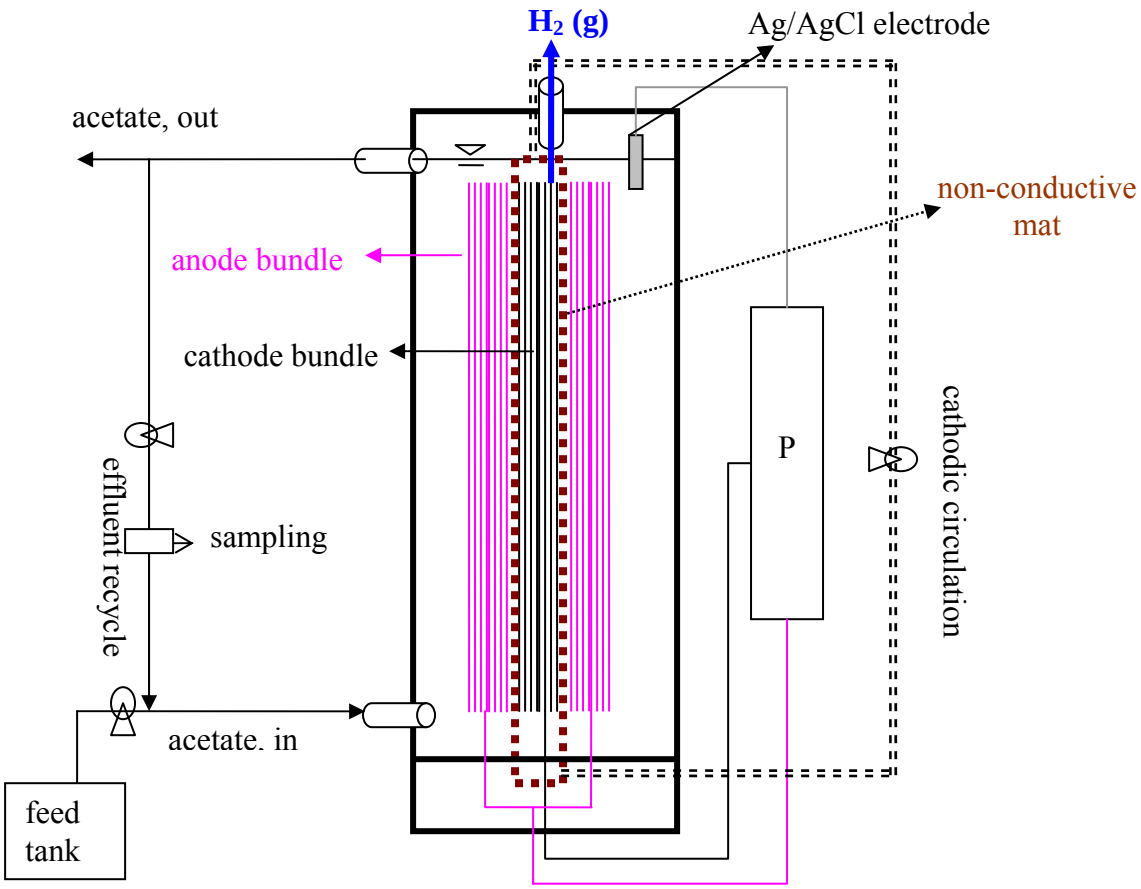

Figure S1. Schematic diagram of the upflow single-chamber MEC using graphite-fiber bundles as electrodes. P – a potentiostat for power supply. We separated the cathode bundle from the anodes using a non-conductive mat.

2. An Equivalent Circuit

To measure ohmic resistance in the single-chamber microbial electrolysis cell (MEC), we performed electrochemical impedance spectroscopy (EIS) using a potentiostat. We analyzed impedance spectra at a fixed anode potential = +0.07V (vs. SHE) for a closed-circuit system. We varied the frequency from 100 kHz to 10 mHz with an alternating-current signal of 10 mV amplitude. We recorded the impedance spectra when the anode was the working electrode, the cathode was the counter electrode, and Ag/AgCl was the reference electrode. We analyzed EIS data with an electrical circuit (Figure S2) that is comprised of an ohmic-resistance component and a constant-phase element in parallel with a resistance combining charge-transfer with diffusion. To accurately estimate ohmic resistance, we fit the EIS data with a Levenberg-Marquardt non-linear least square algorithm in EC lab software (Version 9.5).

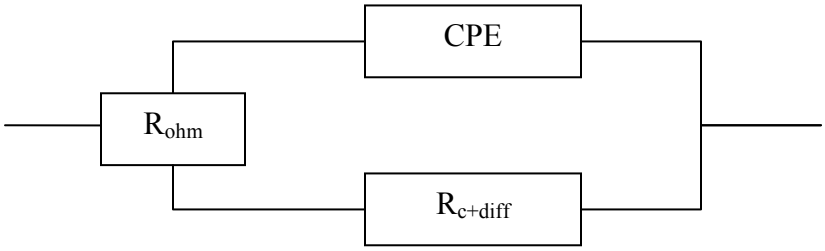

Figure S2. An equivalent circuit used for impedance analyses. R_{ohm}: ohmic resistance, CPE is a double layer constant phase element, and R_{c+diff} is sum of charge transfer resistance and diffusion resistance.

3. Measurement of Dissolved H_2 Concentration

We measured dissolved H_2 concentration in the steady-state continuous MEC in order to quantify H_2 loss from effluent discharge. We directly sampled 1 mL of liquid from the MEC with a sterile syringe and moved the sample into a 5-mL glass tube capped with butyl rubber stopper that had been sparged with ultrapure N_2 gas (99.999%) for 30 min. Then, we placed the glass tube in a 30°C incubation shaker for 3 days to establish equilibrium between liquid and gas phases; we carried out control test with the glass tube in the same condition without injecting liquid sample and used its measured H_2 gas concentration as the blank. We quantified H_2 gas concentration in headspace with a trace analytical gas chromatograph (ta 3000, Ametek) using a reduction gas detector and ultra purity N_2 (99.999%) as a carrier gas at a pressure of 90 psig. Standard H_2 gas (100 ppm, Matheson Trigas) was used for establishing calibration curves by blending with N_2. We measured dissolved H_2 concentration of the MEC in duplicate for each HRT.

4. Gas Composition in the Single-chamber MEC.

We monitored gas composition in the continuous single-chamber MEC. Figure S3 shows that H_2 gas composition was very stable at 49-53%, and CH_4 fraction of gas was small at 1.8-6.9% with HRT varied. The small, but consistent CH_4 production, despite the short HRT, suggests accumulation of methanogens on the electrodes, which means that we cannot suppress methanogenesis in a continuous single-chamber MEC by controlling hydraulic retention time.

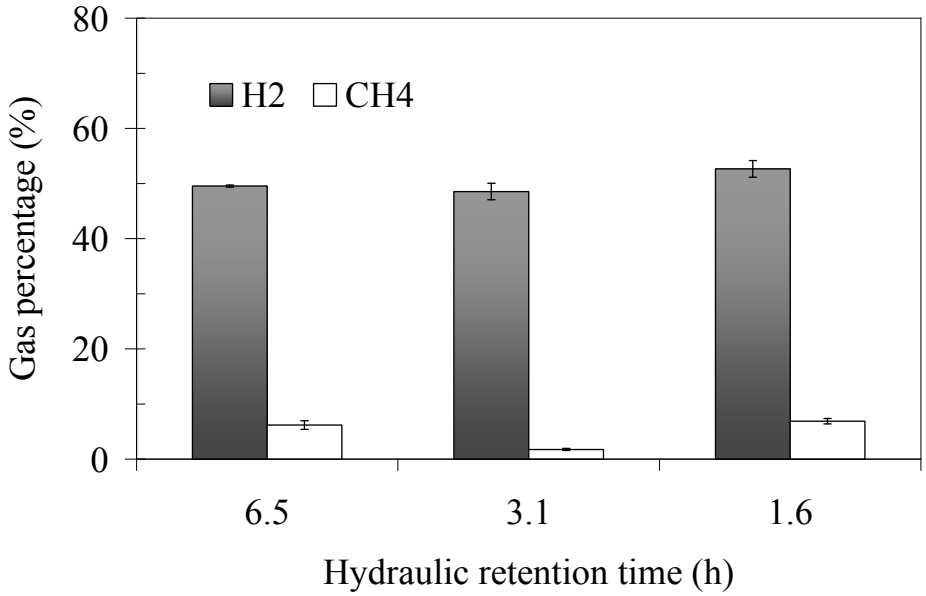

Figure S3. Percentages of H_2 and CH_4 gases in the single-chamber MEC for different HRTs.

5. Characterization of Current Density from Acetate and H_2.

We estimated distributions of current density produced from acetate and H_2 given that the true coulombic efficiency (CE) for acetate is 90%, which is close to the maximum CE reported from MFC/MEC studies (*1*). To characterize current density, we subtracted 0.9 times the current density associated with acetate utilization from the observed current density for quantifying the current density from H_2 oxidation. As seen in Figure S4, the current density from acetate oxidation was 47%, 40%, and 29% of observed current density, respectively, for HRT 1.6, 3.1, and 6.5 h. This characterization supports that anode-respiring bacteria in our single-chamber MEC preferred H_2 to acetate as electron donor and that the H_2 recycle effect was very significant for current generation.

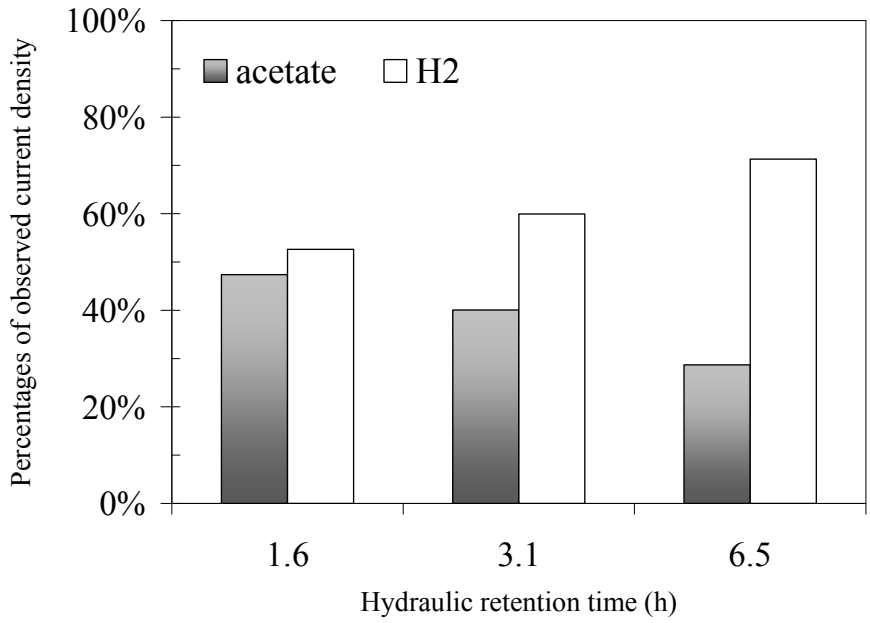

Figure S4. Distributions of coulombs generated from acetate and H_2 in the single MEC given that CE is 90% for acetate.

6. Quantification of Ohmic Resistance

Figure S5 presents Nyquist plots in duplicate experiments at HRT 1.6 h and anode potential -0.03V (vs standard hydrogen electrode). Read values of ohmic resistance were ~ 0.38 Ω, but average of ohmic resistances estimated by the Levenberg-Marquardt non-linear least square algorithm using EC lab software were 0.49 Ω. Either result supports that eliminating membrane from MEC systems can almost totally eliminate ohmic resistance.

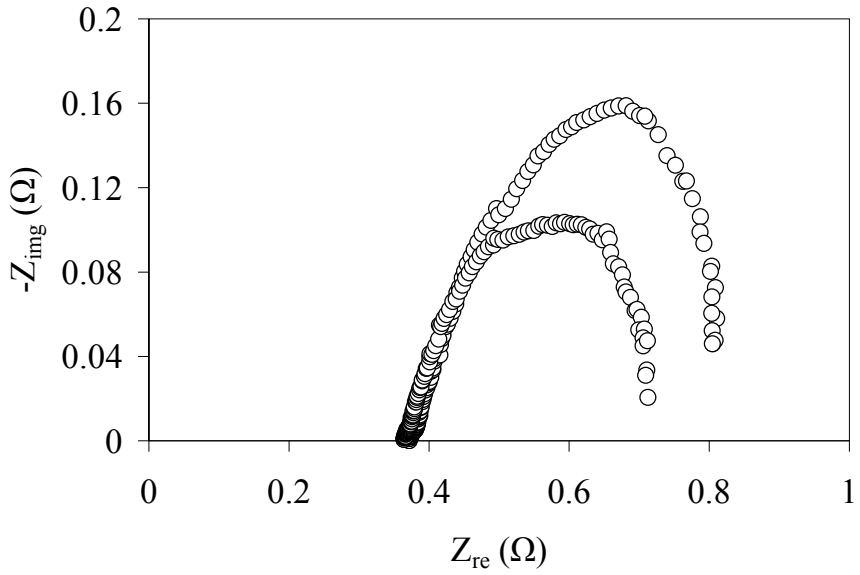

Figure S5. Nyquist plots for the single MEC operated at 1.6 h of HRT and E_{anode} fixed at -0.03 V. Current was 0.195-0.208 A (1,560-1,662 A/m^3).

7. Characterization of Anode and Cathode Over-potentials.

We computed anode and cathode over-potentials, based on standard potential for reducing half-reactions for acetate and water at pH 7.

The anode reaction for acetate oxidation is:

$1/8\ CO_2 + 1/8\ HCO_3^- + H^+ + e^- = 1/8\ CH_3COO^- + 3/8\ H_2O$, $E°'_{acetate} = -0.28V$

The cathode reaction for water molecule reduction is:

$H_2O + e^- = OH^- + 1/2\ H_2$ $E°'_{H2O} = -0.41V$

Anode over-potential (η_{anode}) can be computed by the relation of η_{anode} = anode potential - $E°'_{acetate}$. Due to a fixed anode potential at -0.126 V vs. SHE, anode over-potential was calculated by

Anode over-potential = (-0.126) – (-0.28) = 0.154 V

Cathode over-potential ($\eta_{cathode}$) was calculated by the relation of $\eta_{cathode} = E°'_{H2O}$ − cathode potential. Since cathode potentials varied with current density in our experiments, cathode over-potential changed slightly with HRT. We summarize all over-potentials and applied voltage for each HRT in Table S1.

Table S1. Characterization of electrode over-potentials, ohmic energy losses, and measured applied voltage for each HRT

HRT (h)	η_{anode} (V)	$\eta_{cathode}$ (V)	η_{ohmic} (V)	Applied voltage (V)
6.5	0.154	1.15 ± 0.07	0.090 ± 0.003	1.43 ± 0.04
3.1	0.154	1.19 ± 0.05	0.097 ± 0.002	1.47 ± 0.05
1.6	0.154	1.21 ± 0.03	0.1 ± 0.003	1.49 ± 0.03

η_{anode}: anode over-potential (V), $\eta_{cathode}$: cathode over-potential (V), and η_{ohmic}: ohmic energy loss (V).

Total energy losses were computed to be 1.39 V – 1.46 V, while total energy losses range from 1.3V – 1.4V, based on theoretical standard potential of 0.13 V for $CH_3COO^- + 3\ H_2O = CO_2 + HCO_3^- + 4\ H_2$ at pH 7. A small error (~0.1 V) can occur because we did not account for temperature and constituents' concentration in these computations. Characterization of over-potentials and ohmic energy losses clearly shows that cathode over-potential was the main energy loss in our single-chamber MEC lacking metal catalyst on the cathode.

8. Estimation of H_2 Production Rate to Applied Voltage at CCE = 100%

We calculated H_2 production rate from the single-chamber MEC given that no H_2 recycle and methanogenesis occur in the MEC (CCE=100%). To provide current density data for different applied voltages, we decreased anode potential from -0.126 to -0.326 V (vs. standard hydrogen electrode) in a potentiostat mode. For steady-state acetate concentration, we converted average of current density into H_2 production rate at each applied voltage. Using linear regression, we obtained the equation y =15.632x - 5.0988 where y is H_2 production rate (m^3 H_2/m^3-d) and x is applied voltage (V).

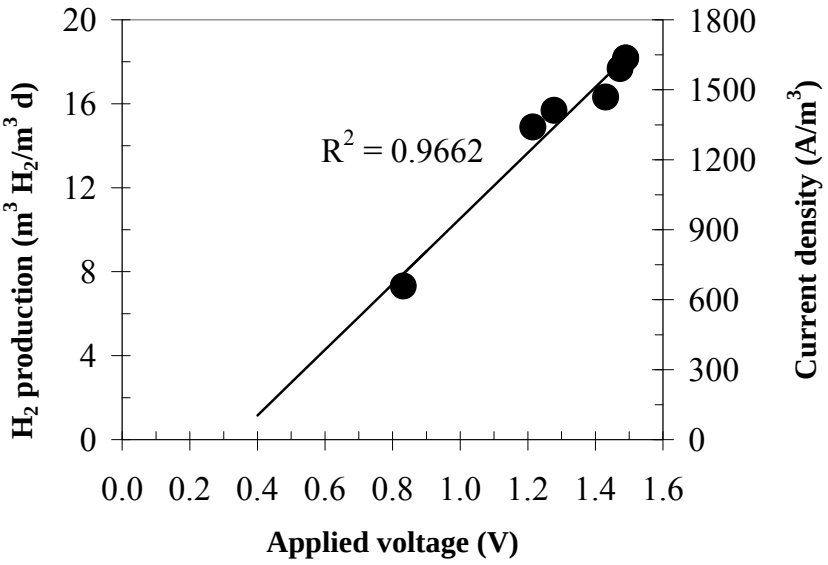

Figure S6. Linear regression for H_2 production rate (volumetric current density) and applied voltage at CCE (cathodic conversion efficiency) of 100%.

Figure S7 compares the estimated and observed H_2-production rates against the applied voltage. Applied voltage required for generating 4.32 m^3 H_2/m^3-d is only 0.6 V, while observed applied voltage for this H_2 production was 1.49 V. This comparison indicates that H_2 recycle can increase applied voltage up to 0.9 V more than its minimum requirement.

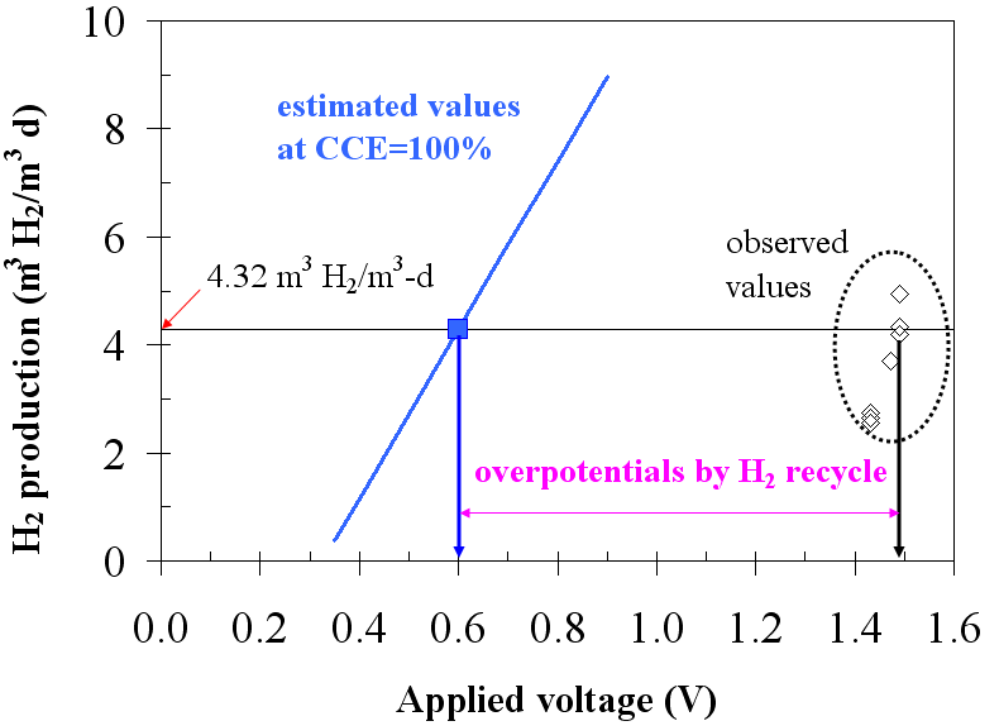

Figure S7. Correlations between H_2 production rate and applied voltage with and without H_2 recycle and CH_4 formation.

Literature Cited

1. Bond, D. R.; Lovley, D. R. Electricity Production by *Geobacter sulfurreducens* Attached to Electrodes. *Appl. Environ. Microbiol.* **2003,** *69* (3), 1548-1555.