

# Hydrogen production from inexhaustible supplies of fresh and salt water using microbial reverse-electrodialysis electrolysis cells

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There is a tremendous source of entropic energy available from the salinity difference between river water and seawater, but this energy has yet to be efficiently captured and stored. Here we demonstrate that H<sub>2</sub> can be produced in a single process by capturing the salinity driven energy along with organic matter degradation using exoelectrogenic bacteria. Only five pairs of seawater and river water cells were sandwiched between an anode, containing exoelectrogenic bacteria, and a cathode, forming a microbial reverse-electrodialysis electrolysis cell. Exoelectrogens added an electrical potential from acetate oxidation and reduced the anode overpotential, while the reverse electro-dialysis stack contributed 0.5–0.6 V at a salinity ratio (seawater:river water) of 50. The H<sub>2</sub> production rate increased from 0.8 to 1.6 m<sup>3</sup>-H<sub>2</sub>/m<sup>3</sup>-anolyte/day for seawater and river water flow rates ranging from 0.1 to 0.8 mL/min. H<sub>2</sub> recovery, the ratio of electrons used for H<sub>2</sub> evolution to electrons released by substrate oxidation, ranged from 72% to 86%. Energy efficiencies, calculated from changes in salinities and the loss of organic matter, were 58% to 64%. By using a relatively small reverse electro-dialysis stack (11 membranes), only ~1% of the produced energy was needed for pumping water. Although Pt was used on the cathode in these tests, additional tests with a nonprecious metal catalyst (MoS<sub>2</sub>) demonstrated H<sub>2</sub> production at a rate of 0.8 m<sup>3</sup>/m<sup>3</sup>/d and an energy efficiency of 51%. These results show that pure H<sub>2</sub> gas can efficiently be produced from virtually limitless supplies of seawater and river water, and biodegradable organic matter.

electrohydrogenesis | microbial electrolysis cell | microbial fuel cell | renewable energy | sustainable energy

Exoelectrogenic bacteria oxidize organic matter and can transfer electrons to electrically conductive materials such as graphite or metal, making it possible to convert waste organic matter into useful energy. In microbial fuel cells (MFCs), exoelectrogens on the anode, coupled with oxygen reduction at the cathode, can generate a potential as large as ~0.8 V (open circuit; pH 7; 0.2 atm O<sub>2</sub>), although less voltage (~0.23 to 0.5 V) is generated in practice (1). Exoelectrogens can also be used to drive electrochemical H<sub>2</sub> production in a microbial electrolysis cell (MEC) (2, 3). However, the potential generated by substrate oxidation (–0.30 V vs. Standard Hydrogen Electrode; 1 g/L acetate; pH 7) is not sufficient to drive H<sub>2</sub> evolution (–0.41 V vs. Standard Hydrogen Electrode at pH 7) (1). Thus, additional energy (~0.11 V in theory) is needed to overcome this thermodynamic threshold, and an external voltage of >0.4 V is typically applied to MECs (4). This additional energy could be provided by a renewable source of energy, such as solar (5), wind, or waste organic matter (6). However, no method has yet been developed to directly achieve H<sub>2</sub> production in one process without an external voltage supply.

Reverse electro-dialysis (RED) holds great promise as a method for generating electricity from the salinity gradient between seawater and river water (7). RED systems are built as stacks of alternating cation- and anion-exchange membranes situated

between two electrodes. When seawater and river water are provided into the RED stack, counter-ions (selected ions) to the membranes are driven from seawater to river water due to the salinity difference, creating an electric potential across the ion-exchange membrane. Each pair of anion- and cation-exchange membranes can in theory create 0.155 V for a salinity ratio of 50 between seawater and river water (based on the open circuit potential). Thus, a RED stack requires a minimum at least eight cell pairs to produce current, based on the thermodynamic threshold for water electrolysis (1.23 V). In practice, however, the required number of cell pairs is much larger due to energy losses by Ohmic resistance and electrode overpotentials. Reported resistivity values in RED systems range from 35 to 65 Ω-cm<sup>2</sup> per cell pair for salinity ratios of 30 to 100 (8–10). Assuming roughly a 50% loss in efficiency due to electrode overpotentials, a hypothetical RED system would require ~20 cell pairs for H<sub>2</sub> production at 0.5 mA/cm<sup>2</sup>. The voltage produced in a RED stack can be increased by adding cell pairs. However, this addition of cell pairs increases capital costs mainly for ion-exchange membranes and reduces energy recovery due to solution pumping. For example, a 50-cell paired RED system produced 3 V, but the energy loss for pumping was ~25% of the gross power production (10); in a 25-cell paired RED system, the overpotential loss for water electrolysis was 1 to 2 V (11). Alternative redox couples have been suggested to reduce electrode overpotentials in RED systems (10, 12). However, chemicals such as Fe(CN)<sub>6</sub><sup>4-</sup>/Fe(CN)<sub>6</sub><sup>3-</sup> can result in toxic HCN gas production under extreme redox conditions at the electrodes, and chemicals such as Fe<sup>2+</sup>/Fe<sup>3+</sup> can result in undesirable precipitation on electrode surfaces. Thus, it is not possible to generate current or achieve hydrogen gas production using a RED system without a large number of membranes.

A unique method of H<sub>2</sub> production is demonstrated here based on integrating a very small (five membrane pairs) RED stack into a microbial electrolysis cell, where anodic oxidation of organic matter is driven by exoelectrogenic microorganisms. In this microbial reverse-electrodialysis electrolysis cell (MREC), H<sub>2</sub> production is achieved by two driving forces: a thermodynamically favorable oxidation of organic matter by exoelectrogens on the anode; and the energy derived from the salinity gradient between seawater and river water. Individually, neither of these systems can accomplish hydrogen gas generation: the MEC requires an energy input (added voltage); and a small RED stack by itself cannot produce current. As stand-alone systems, a much larger RED stack than that used in this study would be needed to power the MEC. However, in this integrated system, the exoelectrogens on the anode produce current and create a favorable reaction, and thus substantially reduce the electrode overpotential. The added salinity driven energy, provided by using only a

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small number of RED cell pairs, completely eliminates the need for an external power source for the MEC. The use of a small number of RED cell pairs, coupled with an optimized flow scheme, also minimizes energy losses for pumping solutions. The MREC therefore represents a unique method for generating H<sub>2</sub> from relatively unlimited energy sources: organic matter in solution, for example in domestic and industrial wastewaters, and seawater and river water.

## Results and Discussion

**MREC Operation.** The MREC, constructed with five pairs of seawater and river water cells, produced from 21 to 26 mL of gas over each fed-batch cycle (Fig. 1A). The produced gas was pure H<sub>2</sub>, with no detectable CH<sub>4</sub> or CO<sub>2</sub> gases. Increasing the water flow accelerated H<sub>2</sub> production, because the salinity gradient was maintained between the seawater and river water cells throughout the RED stack. The increase in H<sub>2</sub> production from an increase in water flow from 0.4 to 0.8 mL/min was smaller than that obtained when increasing the flow from 0.1 to 0.4 mL/min, however, suggesting that further increases in the flow would not substantially increase H<sub>2</sub> production. There was a slightly larger rate of H<sub>2</sub> production using the cathode constructed around a stainless steel current collector (SS) than a more expensive carbon cloth (CC) cathode (13).

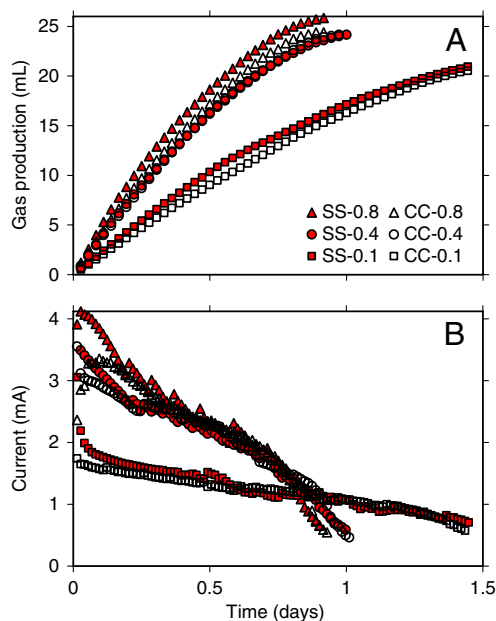
The maximum electrical current in the MREC was observed at the beginning of the fed-batch cycle, and the current decreased over time as the substrate was depleted (Fig. 1B). Current densities were similar for water flow rates between 0.8 and 0.4 mL/min, but substantially smaller currents were obtained at 0.1 mL/min. As a result of slower oxidation of substrate, the fed-batch cycle increased from ~0.9 to ~1.4 d with the decreased water flow rate. The current was almost identical in the later part of the cycle (after 0.2 d) with the CC and SS cathodes, but the SS cathode produced slightly greater current in the earlier part of the cycle.

The substrate removal was 85 ± 6% (*n* = 6) on the basis of COD (chemical oxygen demand) removal over a fed-batch cycle. As the acetate was oxidized, protons were released in the anode chamber, resulting in a pH decrease from 7.0 to 5.2 ± 0.1 even with the use of a pH buffer. This low pH was responsible for the incomplete removal of COD as it is known that exoelectro-

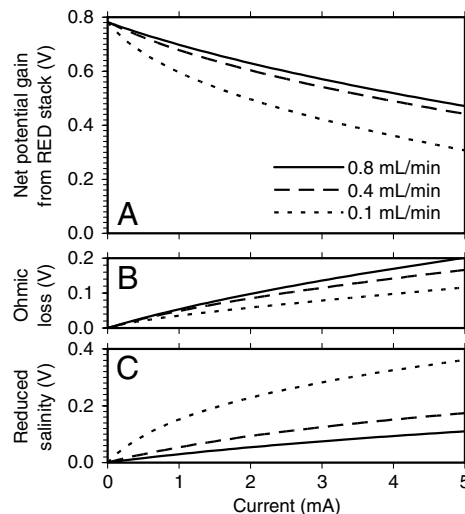
genic activity is significantly inhibited at a pH of ~5 (14). There was a much larger catholyte pH increase over a cycle (from 6.1 ± 0.2 to 12.3 ± 0.1) due to the absence of a buffer. According to the Nernst equation, a unit increase in the catholyte pH increases the equilibrium potential for H<sub>2</sub> evolution by 0.06 V. This correlation between pH and equilibrium potential implies, for instance, that further increase in the catholyte pH up to 13 would result in little decrease in MREC performance. Thus, the low anolyte pH is considered to be the main reason for the termination of current production at the end of the fed-batch cycle. In future designs it should be possible to recirculate a smaller volume of a high pH catholyte into a larger-volume anode chamber to better control pH conditions. This catholyte addition would also have the advantage of slightly increasing the solution conductivity and reducing Ohmic losses in the anode chamber.

**Voltage Contribution by RED.** The five-cell paired RED stack was estimated to contribute 0.5–0.6 V for H<sub>2</sub> production (Fig. 2A) using Eqs. 2–4 and the observed ion flux efficiency ( $\eta_{\text{flux}} = 0.81 \pm 0.06$ , *n* = 6). This ion flux efficiency corresponds to a transport number of the counter-ion ( $t_{\text{counter}}$ ) of ~0.91, indicating there was no failure in membrane integrity or permselectivity. During the experiments with water flow rates of 0.4 or 0.8 mL/min, ~80% of the H<sub>2</sub> was produced at a current between 2 and 4 mA (Fig. 1). Similarly, at a water flow rate of 0.1 mL/min, the majority of the H<sub>2</sub> production was achieved at a current of 1 to 2 mA. For these current ranges, the corresponding voltage contribution by the RED stack was 0.5–0.6 V for all three applied flows (Fig. 2A).

The decrease in the RED voltage with increasing current is due to two factors: a resistive Ohmic loss; and the reduction in the salinity gradient as the water flows through the membrane stack. Ohmic losses increased at higher flow rates due to the influent river water salinity being maintained throughout the RED stack (Fig. 2B). As a result, smaller changes in the salinity gradient along the flow through the stack provide greater energy available for current generation (Fig. 2A). An increase in flow rate from 0.1 to 0.4 mL/min substantially reduced voltage losses due to less change in the initial salinity gradient as the water flowed through the stack (Fig. 2C), resulting in a significant improvement in the net RED voltage (Fig. 2A). However, with an increase in flow rate from 0.4 to 0.8 mL, the increase in the net RED voltage was relatively small because an improvement in maintaining the overall salinity gradient was offset by an increase in Ohmic losses.



**Fig. 1.** Effects of solution flow (0.1, 0.4, and 0.8 mL/min) and current collector (SS: stainless steel, CC: carbon cloth) on (A) gas production, (B) current generation.



**Fig. 2.** The RED stack voltage calculated by Eqs. 2–4 ( $\eta_{\text{flux}} = 0.81$ ): (A) net potential from the stack; (B) Ohmic losses; and (C) voltage losses due to a reduction in the initial salinity gradient.



and current generation from organic matter reduced the required number of seawater and river water cells that would be needed to drive  $H_2$  evolution at the cathode, making the combined process much more efficient than an individual RED process. By using a small RED stack, energy consumption for water pumping was negligible compared to the produced energy as  $H_2$ . Because practical applications of RED have been limited due to the need for stacks with hundreds ion-exchange membranes, this unique MREC process could be used to more efficiently produce  $H_2$  from an estimated 1.7 TW of global salinity driven energy (18).

The MREC can be used not only as a method for  $H_2$  production, but also as a method of wastewater treatment. Even though this study was conducted under well controlled conditions with acetate as substrate, exoelectrogens can use various sources of organic matter, ranging from domestic and animal wastewaters to industrial wastewaters (19). The anode chamber was operated as a fed-batch reactor here, but wastewater can also be continuously supplied into the anode chamber, as previously demonstrated with MECs (20, 21). The continuous flow system for wastewater would not affect the  $H_2$  production, because the anode and cathode chamber are completely separated with a stack of ion-exchange membranes. In addition, this separated cathode chamber from wastewater excludes possible losses of  $H_2$  through methanogenesis, which is inevitable in single chamber MECs (17). Thus, this unique type of integrated system has significant potential to treat wastewater and simultaneously produce pure  $H_2$  gas without any consumption of electrical grid energy.

## Materials and Methods

**MREC Construction.** A cubic Lexan block with a cylindrical chamber (~30 mL; 7 cm<sup>2</sup> in cross section) was used for an anode and cathode container, with a glass tube (20 mL) glued to the top of the cathode chamber to collect  $H_2$  (22). The SS cathode was prepared with platinum (0.6 mg/cm<sup>2</sup>; BASF) as the catalyst (except as indicated) in a mixture of carbon black and Nafion on both sides of a 7-cm<sup>2</sup> stainless steel mesh (#50) (13). In some tests the SS cathode was prepared with MoS<sub>2</sub> (6.3 mg/cm<sup>2</sup>) as a replacement of the Pt catalyst. The carbon cloth (CC) cathode was made with a Pt catalyst (0.5 mg/cm<sup>2</sup>) in the same manner using a 7-cm<sup>2</sup> piece of carbon cloth (23). The anode (a graphite fiber brush 2.7 cm in diameter and 2.3 cm in length; Mill-Rose Lab Inc.) was inoculated with the effluent from an existing MFC and initially enriched in a single chamber MFC (24). During this start-up stage, the anode microbes were acclimated to a gradual increase in NaCl concentration to avoid salt inhibition effects due to chloride ion transfer into the anode chamber.

A RED stack was sandwiched between the anode and cathode chambers, and it consisted of five pairs of seawater and river water cells made with

five cation- and six anion-exchange membranes (Selemion CMV and AMV, AGC Engineering Co.) (Fig. 5A). Each cell had a dimension of 4 cm × 2 cm × 1.3 mm, and the corresponding empty bed volume of the stack was 10.4 mL. Seawater flowed serially through every seawater cell, and river water had a similar flow path but in the opposite direction to seawater (Fig. 5A). Each solution was continuously provided into the MREC at a specified rate from 0.1 to 0.8 mL/min. The power required for pumping at the highest water flow rate (0.8 mL/min) was approximated by measuring the head loss through the stack. All experiments were performed at 30 °C in a constant temperature room.

**Solutions.** Synthetic seawater was a 35 g/L NaCl solution, and river water was 0.7 g/L NaCl, creating a salinity ratio of 50. The catholyte (40 mL) was synthetic seawater without any pH buffer, and it was initially purged with N<sub>2</sub>. The anolyte (30 mL) was prepared with 1.0 g/L sodium acetate in a phosphate buffer (9.16 g/L Na<sub>2</sub>HPO<sub>4</sub>; 4.9 g/L NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O; 0.62 g/L NH<sub>4</sub>Cl; 0.26 g/L KCl) with minerals and vitamins (25). The corresponding solution volume of the MREC was 30 + 40 + 10.4 = 80.4 mL. The anolyte and catholyte were replaced every fed-batch cycle, while seawater and river water were continuously supplied (Fig. 5B).

**Measurements.** The produced gas volume from the cathode chamber was measured using a respirometer (AER-208, Challenge Environmental Systems) prior to being collected in a gas bag (100 mL capacity; Cali-5-Bond, Calibrated Instruments Inc.). The gas in the bag and in the cathode headspace was analyzed for H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> by gas chromatography (SRI-310C, SRI Instruments) as previously described (17).

The anode and cathode were connected externally to a 10-Ω resistor to measure current based on the voltage drop using Ohm's law. The voltage drop across the resistor was recorded every 20 min using a multimeter (Keithley Instruments).

Effluent seawater, river water, anolyte, and catholyte solutions were analyzed with conductivity and pH probes (SevenMulti, Mettler-Toledo International Inc.). The anolyte COD was determined according to standard methods (Hach Co.) (26).

**Membrane Permselectivity.** The ion flux efficiency ( $\eta_{flux}$ ) is the fractional contribution of the ion transport to the current and thus it represents the permselectivity of the ion-exchange membranes as:

$$\eta_{flux} = \frac{N_{Cp}i}{zFq(c_{river}^{eff} - c_{river}^{in})}, \quad [1]$$

where  $N_{Cp}$  is the number of cell pairs,  $i$  the current,  $z$  the ionic charge,  $F$  the Faraday constant,  $q$  the solution flow rate, and  $c_{river}$  the NaCl molarity in river water. The superscript *eff* denotes the effluent and *in* the influent to the MREC.

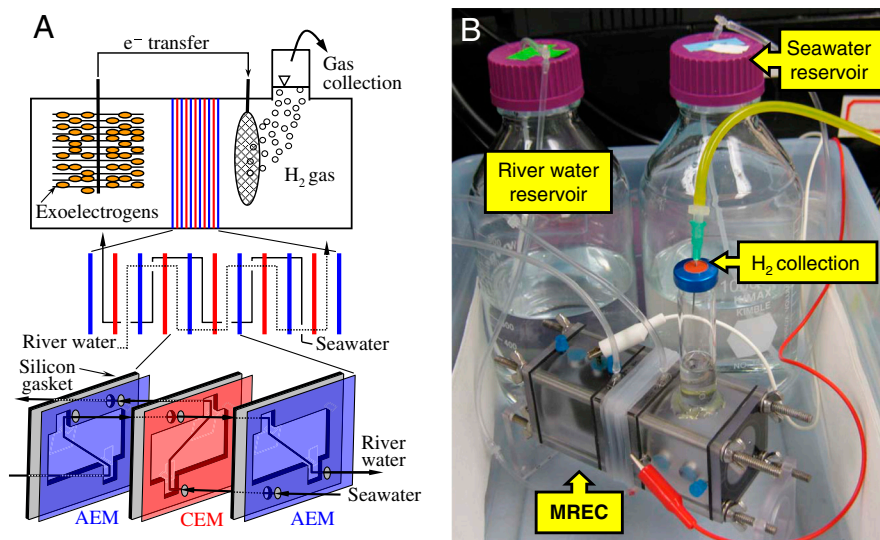


Fig. 5. (A) Schematic design of MREC for  $H_2$  production by integrating exoelectrogens with five-cell paired RED stack. (B) Continuous flow and  $H_2$  collection for MREC operation. The pump and effluent reservoirs are not shown.

**Calculations on RED.** The voltage added by the RED stack equals the sum of the junction potentials created by the salinity difference minus the sum of Ohmic losses. The junction potential across an ion-exchange membrane ( $\Delta\phi_{\text{ict}}$ ) quantifies the salinity driven energy between seawater and river water as (27)

$$|\Delta\phi_{\text{ict}}| = \frac{RT}{zF} \left[ t_{\text{counter}} \ln \left( \frac{a_{\text{counter}}^{\text{sea}}}{a_{\text{counter}}^{\text{river}}} \right) - t_{\text{co}} \ln \left( \frac{a_{\text{co}}^{\text{sea}}}{a_{\text{co}}^{\text{river}}} \right) \right], \quad [2]$$

where  $R$  is the gas constant and  $T$  the absolute temperature. For counter- and co-ions to the ion-exchange membrane,  $t$  is the transport number defined as the fractional contribution of the ionic flux to the current density in the membrane, and  $a$  is the chemical activity. The chemical activity was calculated by multiplying the molar concentration by the activity coefficient ( $f_i$ ). The activity coefficient was calculated as (28)

$$\log f_i = -\frac{A|z_i|^2\sqrt{I_S}}{1 + Ba^0\sqrt{I_S}} - \log(1 + 0.018m_i) + K_i I_S. \quad [3]$$

The Debye-Hückel constants were  $A = 0.5085 \text{ kg}^{1/2}/\text{mol}^{1/2}$  and  $B = 0.3282 \text{ \AA kg}^{1/2}/\text{mol}^{1/2}$ . The ion size parameter ( $a^0$ ) was  $0.78 \text{ \AA}$  for both sodium and chloride, while  $K_{\text{Na}} = 0.105$  and  $K_{\text{Cl}} = -0.009 \text{ kg}^2/\text{mol}^2$ .  $I_S$  is the ionic strength in molality, and  $m$  the molal concentration. This equation is valid for a NaCl solution up to 1.2 molality (28).

The NaCl concentration was assumed to be homogeneous in each cell, while the concentration change between cells along the flow ( $\Delta c_{\text{cell}}$ ) was determined by:

$$\Delta c_{\text{cell}} = \frac{i}{zqF\eta_{\text{flux}}}. \quad [4]$$

Ohm's law was employed for the resistive loss in each of the solution and membrane phases. Effect of the boundary layer near the membrane surface was ignored due to relatively low current densities (29). The membrane resistivity was  $3.0 \text{ (CMV)}$  and  $2.8 \text{ } \Omega\text{cm}^2 \text{ (AMV)}$  (30).

**H<sub>2</sub> Recovery.** The Coulombic recovery ( $r_{\text{CE}}$ ) is the fraction of the transferred electron to the anode among the total electron released by substrate oxidation (4), and is calculated as

$$r_{\text{CE}} = \frac{8 \int idt}{FV_{\text{An}}\Delta\text{COD}}, \quad [5]$$

where  $V_{\text{an}}$  is the anolyte volume and  $\Delta\text{COD}$  is the removed COD as O<sub>2</sub>.

The cathodic H<sub>2</sub> recovery ( $r_{\text{cat}}$ ) represents the contribution of the mole-H<sub>2</sub> evolution ( $n_{\text{H}_2}$ ) to the total cathodic charge transfer as (4)

$$r_{\text{cat}} = \frac{2n_{\text{H}_2}F}{\int idt}. \quad [6]$$

The overall H<sub>2</sub> recovery ( $r_{\text{H}_2}$ ) is determined by  $r_{\text{H}_2} = r_{\text{CE}}r_{\text{cat}}$ , meaning the ratio of the produced H<sub>2</sub> to the removed organic matter on the electron basis.

The H<sub>2</sub> Yield ( $Y_{\text{H}_2}$ ) is defined on the mole basis as (4)

$$Y_{\text{H}_2} = \frac{32n_{\text{H}_2}}{V_{\text{an}}\Delta\text{COD}}. \quad [7]$$

The maximum volumetric H<sub>2</sub> production rate at 1 atm ( $Q_{\text{H}_2}$ , m<sup>3</sup>-H<sub>2</sub>/m<sup>3</sup>-V<sub>an</sub>/d) was calculated with averaged current ( $i_{\text{avg}}$ ) over the first 1 h of a fed-batch cycle as (4)

$$Q_{\text{H}_2} = \frac{i_{\text{avg}}r_{\text{cat}}RT}{2V_{\text{an}}F}. \quad [8]$$

**Energy Recovery and Efficiency.** The energy recovery ( $r_E$ ) is the combustion energy of the produced H<sub>2</sub> normalized by the total energy provided to the MREC as:

$$r_E = \frac{\Delta H_{\text{H}_2}n_{\text{H}_2}/t_B}{\Delta H_s n_s^{\text{in}}/t_B + X^{\text{in}}}, \quad [9]$$

where  $\Delta H$  is the heat of combustion (J/mol),  $t_B$  the time span for each batch cycle, and  $X^{\text{in}}$  the theoretical energy (W) estimated by the change in the free energy involving complete mixing of seawater and river water as (31)

$$X^{\text{in}} = 2qRT \left( c_{\text{river}}^{\text{in}} \ln \frac{a_{\text{river}}^{\text{in}}}{a_{\text{mixed}}^{\text{in}}} + c_{\text{sea}}^{\text{in}} \ln \frac{a_{\text{sea}}^{\text{in}}}{a_{\text{mixed}}^{\text{in}}} \right). \quad [10]$$

The energy efficiency ( $\eta_E$ ) is defined similarly but by subtracting the energy leaving the MREC (superscript out) from the provided energy as:

$$\eta_E = \frac{\Delta H_{\text{H}_2}n_{\text{H}_2}/t_B}{\Delta H_s (n_s^{\text{in}} - n_s^{\text{out}})/t_B + X^{\text{in}} - X^{\text{out}}}. \quad [11]$$

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