Microbial reverse-electrodialysis chemical-production cell for acid and alkali production

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A new type of bioelectrochemical system, called a microbial reverse-electrodialysis chemical-production cell (MRCC), was developed to produce acid and alkali using energy derived from organic matter (acetate) and salinity gradients (NaCl solutions representative of seawater and river water). A bipolar membrane (BPM) was placed next to the anode to prevent Cl⁻ contamination and acidification of the anolyte, and to produce protons for HCl recovery. A 5-cell paired reverse-electrodialysis (RED) stack provided the electrical energy required to overcome the BPM over-potential (0.3–0.6 V), making the overall process spontaneous. The MRCC reactor produced electricity (908 mW/m²) as well as concentrated acidic and alkaline solutions, and therefore did not require an external power supply. After a fed-batch cycle, the pHs of the chemical product solutions were 1.65 ± 0.04 and 11.98 ± 0.10, due to the production of 1.35 ± 0.13 mmol of acid, and 0.59 ± 0.14 mmol of alkali. The acid- and alkali-production efficiencies based on generated current were 58 ± 3% and 25 ± 3%. These results demonstrated proof-of-concept acid and alkali production using only renewable energy sources.

1. Introduction

A microbial fuel cell (MFC) is a bioelectrochemical system that can produce electrical power from organic matter such as that in domestic and industrial wastewaters [1,2]. Exoelectrogenic microorganisms oxidize organic matter and release electrons to the anode. Electrons flow through an external circuit to the cathode, where oxygen is typically reduced to form water. In the past decade, the power densities of MFCs with air-cathodes have been significantly improved from a few milliwatts per square meter of electrode to 4.3 W/m² [3–5], providing a new source of electrical power for a variety of uses [6].

A microbial reverse-electrodialysis cell (MRC) is a system that combines an MFC with a reverse-electrodialysis (RED) stack [7,8]. RED is one of several technologies being investigated to produce electrical power from salinity gradients between sea and river water, estimated to be 1.7 TW globally [9]. In a RED stack, charged ions are transported through selective ion-exchange membranes due to the charge being balanced due to water dissociation at the BPM, while protons are produced in the anolyte, and to produce acid and alkali solutions [10]. One of the factors limiting abiotic RED applications is the large electrode over-potential [11]. For example, a RED stack with 25 cell pairs had electrode over-potentials of 2 to 2.5 V [12]. The energy losses due to electrode over-potentials were greatly reduced when an MFC was combined with a RED stack due to the thermodynamically favorable reactions at both electrodes (organic matter oxidation at the anode by bacteria, and oxygen reduction at the cathode).

One of limitations to the performance of an MRC with NaCl in the RED stack is that the anolyte pH can decrease during operation to levels that can substantially reduce current generation by exoelectrogenic microorganisms. Another problem is that the salinity of the anolyte can increase due to the transport of chloride ions from the RED stack into the anode chamber [7,8]. Recently, one study showed that inserting a bipolar membrane (BPM) into a microbial desalination cell (MDC) adjacent to the anode chamber avoided a large decrease in anolyte pH and Cl⁻ ion transport into the anolyte due to the charge being balanced due to water dissociation at the BPM (H₂O → H⁺ + OH⁻) [13]. Moreover, acid was produced in the chamber between BPM and AEM (anion exchange membrane) of desalination chamber, with alkali production occurring in the chamber between the CEM (cation exchange membrane) of the desalination chamber and the cathode [13]. Net electrical power could not be produced in this MDC with an air-cathode, however, due to the large over-potential of the BPM (approximately 0.3–0.6 V), and thus an external power supply (≥0.3 V) was required to provide sufficient potential to drive desalination. For optimum acid and alkali production, 1 V was applied to the system.

The objective of this study was to produce acid and alkali without the need for an external power supply by using a BPM in an MRC, in a device called a microbial reverse-electrodialysis chemical-production cell (MRCC) (Fig. 1). To our knowledge BPMs have so far not been used...
solution cells constructed using 5 AEMs and 5 CEMs (Selemion AMV and CMV membranes). Silicon gaskets were placed between adjacent membranes that had rectangular open sections (4 cm width × 2 cm height × 0.13 cm thickness) and polyethylene mesh spacers were used to allow water flow without membrane deformation [7]. The air cathode (projected surface area of 7 cm²) was made of carbon cloth containing four polytetrafluoroethylene (PTFE) diffusion layers on one side, and a 0.5 mg Pt/cm² catalyst layer on the other side, and it was placed in the alkali-production chamber [15].

2.2. Operation and measurements

The anode was preacclimated with exoelectrogenic microorganisms in an MFC originally inoculated with primary clarifier effluent collected from the Pennsylvania State University wastewater treatment plant. After stable voltage production was observed over 30 fed-batch cycles (10 Ω external resistor), the anode was transferred to the MRCC reactor. The anolyte (30 mL) consisted of 1 g/L sodium acetate in a 50 mM phosphate buffered nutrient medium (4.28 g/L Na₂HPO₄, 2.45 g/L NaH₂PO₄·H₂O, 0.31 g/L NH₄Cl, and 0.13 g/L KCl, trace minerals, and vitamins; pH = 7, conductivity = 6.74 mS/cm) [16]. The high concentrate (HC, 35 g/L NaCl, 54 mS/cm) and low concentrate (LC, 0.7 g/L NaCl, 1.4 mS/cm) solutions were prepared with a salinity ratio of 50, and were continuously supplied to the RED stack at a fixed flow rate of 1.6 mL/min at the beginning of each fed-batch cycle. The HC solution flowed serially through 5 HC cells, and LC solution flowed serially through 4 LC cells (Fig. 1). The solutions used in the acid-production and alkali-production chambers were each 60 mL and contained 0.7 g/L NaCl, and they were separately recycled through the acid-production and alkali-production chambers (each with a 7 mL capacity).

A resistor (10 Ω or 300 Ω) was connected between the anode and cathode to measure current using a multimeter (Model 2700, Keithley Instrument). Polarization data were obtained using a potentiostat (Uniscan PG580RM) under galvanostatic conditions (0 mA, 0.2 mA, 0.5 mA, 0.7 mA, 0.9 mA, 1.1 mA, 1.5 mA, 2 mA, and 2.5 mA). Chemical oxygen demand (COD) was measured according to standard methods (Hach Co.). Solution pH was determined using a meter (VWR SB70P) and pH probe (SympHony pH probe), and conductivity was measured using a meter (VWR SB90M5) and probe (SympHony conductivity probe). Chloride concentrations were measured using ion chromatography (Dionex ICS-1100). H⁺ and OH⁻ concentrations were calculated from changes in pH in the acid-production and alkali-production chambers [17]. The acid-production (or alkali-production) efficiencies were calculated based on H⁺ (or OH⁻) concentrations compared to the total recovered coulombs [13].

3. Results and discussion

After the output voltage of the MRCC with a 10 Ω external resistor became stable for three consecutive cycles, a polarization test was performed to evaluate the electrical performance of this system (Fig. 2). The internal resistance was approximately 300 Ω based on the slope of the polarization data. The maximum power density was 908 mW/m², which was comparable to that produced in an MFC [18,19]. The anode potential was extremely stable, varying only over a small range of −0.48 V to −0.44 V vs. Ag/AgCl. Cathode overpotential limited performance, as shown by a decrease in the cathode and RED stack potentials from 0.39 V to −0.34 V vs. Ag/AgCl over the measured current density range of 0 A/m² to 3.5 A/m². These results demonstrated that this system could operate without an external power supply.

Acid and alkali production of the MRCC system was investigated with 300 Ω (peak power conditions) or 10 Ω (limiting current conditions) external resistors. The lower resistor produced a current of 3.5 mA while the higher resistor produced 1.6 mA (Fig. 3A). This
resulted in higher concentrations of acid and alkali solutions with the 10 Ω resistor (Fig. 3B and C) than with the 300 Ω resistor. With a 10 Ω external resistor, the pH of acid-production chamber decreased to 1.65 ± 0.04 and the pH of alkali-production chamber increased to 11.98 ± 0.10 (Fig. 3B). The H⁺ and OH⁻ concentrations at the end of the cycle were 22.5 ± 2.1 mM (H⁺) and 9.8 ± 2.4 mM (OH⁻) (Fig. 3C). On the basis of volumes used for chemical production (60 mL each), the total amounts of acid and alkali production were 1.35 ± 0.13 mmol for acid and 0.59 ± 0.14 mmol for alkali. The acid-production efficiency was 58 ± 3%, while the alkali-production efficiency was 25 ± 3%. The lower alkali-production efficiency might be due to loss of OH⁻ into the RED stack and the low efficiency of oxygen reduction to hydroxyl ions (O₂ + 2H₂O + 4e⁻ → 4OH⁻). These results demonstrated that acid and alkali could be effectively produced using an MRCC without an external power supply.

The anolyte pH and chloride concentrations were very stable despite proton production in the anode chamber and possible Cl⁻ transport from the RED stack. At the end of a fed-batch cycle (23 h), the anolyte pH slightly had decreased from 7.0 ± 0.1 to only 6.74 ± 0.02. In contrast, previous MRC tests without a bipolar membrane reported a pH decrease to 5.5 ± 0.1 [7,8]. There was no appreciable change in Cl⁻ concentrations in the anode solution (from 0.29 ± 0.1 g/L to 0.32 ± 0.01 g/L). These results show that the use of the BPM, in concert with the RED stack, was effective to control anolyte pH and Cl⁻ transfer into the anode chamber.

The acid and alkali production obtained here was only about half that previously reported with 1 V of external applied voltage [13], which was reasonable since only ~0.5 V was generated by the 5 cell-pairs RED stack. The performance could likely be further improved by using more cell pairs. An additional advantage of the RED stack was that it stabilized the anode potentials, enabling power to be produced at a maximum of 908 mW/m². For these reasons, the MRCC system is quite promising for acid and alkali production as it requires only sources of renewable organic matter and salinity gradient energy.

4. Conclusions

Acid and alkali were produced without an external power supply using organic matter and salinity gradient energy in an MRCC. Overall, 1.35 ± 0.13 mmol of acid and 0.59 ± 0.14 mmol alkali were produced in each fed-batch cycle (23 h), with an acid-production efficiency of 58 ± 3% and alkali-production efficiency of 25 ± 3%. Additionally, power was produced due to the inclusion of a RED stack. The anolyte pH was maintained at near-neutral conditions and there was insignificant chloride ion transfer to the anode chamber through the use of a BPM. These results show that the MRCC can produce these commodity chemical streams using only renewable energy sources.
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References