Development of the Microbial Electrolysis Desalination and Chemical-Production Cell for Desalination as Well as Acid and Alkali Productions

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Supporting Information

ABSTRACT: By combining the microbial electrolysis cell and the microbial desalination cell, the microbial electrolysis desalination cell (MEDC) becomes a novel device to desalinate salty water. However, several factors, such as sharp pH decrease and Cl⁻ accumulation in the anode chamber, limit the MEDC development. In this study, a microbial electrolysis desalination and chemical-production cell (MEDCC) was developed with four chambers using a bipolar membrane. Results showed that the pH in the anode chamber of the MEDCC always remained near 7.0, which greatly enhanced the microbial activities in the cell. With applied voltages of 0.3−1.0 V, 62%−97% of Coulombic efficiencies were achieved from the MEDCC, which were 1.5−2.0 times of those from the MEDC. With 10 mL of 10 g/L NaCl in the desalination chamber, desalination rates of the MEDCC reached 46%−86% within 18 h. Another unique feature of the MEDCC was the simultaneous production of HCl and NaOH in the cell. With 1.0 V applied voltage, the pH values at 18 h in the acid-production chamber and cathode chamber were 0.68 and 12.9, respectively. With the MEDCC, the problem with large pH changes in the anode chamber was resolved, and products of the acid and alkali were obtained.

INTRODUCTION

The microbial desalination cell (MDC) is a device to desalinate salty water using electricity generated by the microbial fuel cell (MFC).1 However, the desalination efficiency of the MDC is limited by the fluctuated voltages produced by the exoelectrogenic bacteria.2 Then the microbial electrolysis desalination cell (MEDC) was developed by combining the microbial electrolysis cell (MEC) and the MDC.3,4 In these studies, the MDC and MEDC were composed of an anode chamber, a desalination chamber, and a cathode chamber. An anion exchange membrane (AEM) was installed between the anode chamber and the desalination chamber, and a cation exchange membrane (CEM) was between the desalination chamber and the cathode chamber. It was reported that 98.8% of 10 g/L NaCl and 68% of 20 g/L NaCl were removed using the MEDC, which were 1.5−2.0 times of those from the MEDC. With 10 mL of 10 g/L NaCl in the desalination chamber, desalination rates of the MEDCC reached 46%−86% within 18 h. Another unique feature of the MEDCC was the simultaneous production of HCl and NaOH in the cell. With 1.0 V applied voltage, the pH values at 18 h in the acid-production chamber and cathode chamber were 0.68 and 12.9, respectively. With the MEDCC, the problem with large pH changes in the anode chamber was resolved, and products of the acid and alkali were obtained.

pH decrease in the anode chamber is harmful to the microbial activities because most of bacteria in the cell favor a neutral pH condition.5,6 The microbial metabolism in the anode chamber can be inhibited at low pH values, resulting in low current density.7,8 To avoid sharp pH changes in the chamber, Cao et al.1 replaced the anolyte every 12 h and Chen et al.5 replaced the anolyte twice in one desalination cycle. Second, the Cl⁻ accumulation in the anode chamber can dramatically increase because Cl⁻ ions transfer from the middle chamber to the anode chamber to balance the protons produced by the exoelectrogenic bacteria. The Cl⁻ accumulation in the anode chamber may also inhibit the bacterial activities.4 Third, a high phosphate buffer solution (50 mM) used in the MDC or MEDC3,4 may result in phosphate groups transferring through the AEM to the desalination chamber. The phosphate transfer may cause heavy deposit of Mg²⁺ and Ca²⁺ in the desalination chamber during the treatment of seawater or brine water.

Bipolar membrane (BPM) has been successfully used in many chemical processes, such as separation of ions from the corresponding salts, electroextraction, back-extraction, purifica-

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tion of acid and bases, and production of organic acids and soy protein isolates. With an electric field in the BPM, the water dissociation reaction occurs between the two layers, in which H\(^+\) migrates through the cation exchange layer and OH\(^-\) migrates through the anion exchange layer. To control pH changes in the anode chamber, eliminate the negative effects of Cl\(^-\) and phosphate, and reclaim Na\(^+\) in the cell, we propose a new device using BPM. The device is called the microbial electrolysis desalination and chemical-production cell (MEDCC). The device consists of four chambers: an anode chamber, an acid-production chamber, a desalination chamber, and a cathode chamber (alkali-production chamber) (Figure 1A,B). A CEM is installed between the cathode and a cathode chamber (the alkali-production chamber) (Figure 1A,B). A CEM is installed between the cathode chamber and the desalination chamber, an AEM between the desalination chamber and the acid-production chamber, and a BPM between the acid-production chamber and the anode chamber. With an electric field in the system, the process of water dissociation takes place with the BPM. H\(^+\) ions migrate into the acid-production chamber to produce acid and OH\(^-\) ions migrate into the anode chamber to keep the pH neutral, promoting microbial activities in the cell. At the same time, cations in the desalination chamber move to the cathode chamber. The electrons pass through the external circuit and oxygen diffuses into the cathode chamber. The reaction \(O_2 + 2H_2O + 4e^- \rightarrow 4OH^-\) occurs in the cathode chamber. The cations combine with OH\(^-\) to produce alkali in the cathode chamber. Anions in the desalination chamber move into the acid-production chamber and combine with H\(^+\) to produce acid. Through these processes, salty water is desalinated without any phosphate leakage, the problem with large pH changes in the chambers is resolved, and products of acid and alkali are obtained in the MEDCC.

The aim of this study was to demonstrate the advantages of the MEDCC over the MEDC as well as the electrolysis desalination and chemical-production cell (EDCC). Specifically, desalination rates, Coulombic efficiencies, acid- and alkali-production performances of these three types of reactors were measured and compared. Efficiencies of acid-production and alkali-production were also discussed.

### MATERIALS AND METHODS

#### Reactor Construction.
The MEDCC reactor was made of poly(tetrafluoroethylene). Each electrode chamber was constructed by drilling a hole with a diameter of 3 cm in a solid poly block. The available volumes of the cathode chamber, the desalination chamber, the acid-production chamber, and the anode chamber were 30, 10, 10, and 30 mL, respectively. CEM (Ultrex CMI-7000), AEM (Ultrex AMI-7001), and BPM (Fumasep-FBM) were used for the construction. Graphite brush (25 mm diameter \(\times\)30 mm length) was used as the anode. The cathode consisted of a 30% wet-proofed carbon cloth with platinum (0.5 mg/cm\(^2\)) and four diffusion layers on it with the effective surface area of 7 cm\(^2\) (3 cm in diameter) (Figure 1A,B). For comparison, the MEDC and the EDCC were also constructed. The structure of the MEDC was almost the same as that of the MEDCC, but without the acid-production chamber and the BPM. The structure of the EDCC was the same as that of the MEDCC, but without adding microbes in the anode chamber during the operation.

#### Medium and Operation.
Ten milliliter effluent of matured single-chamber MFC anolyte was inoculated in the anode chambers of the MEDCC and MEDC. The anodic solution for the MFC, MEDCC, MEDC, and EDCC contained (in 1 L deionized water) 1 g of CH\(_3\)COONa, 4.0896 g of Na\(_2\)HPO\(_4\), 2.544 g of NaH\(_2\)PO\(_4\), 0.31 g of NH\(_4\)Cl, 0.13 g of KCl, 12.5 mL of trace metal solution, and 12.5 mL of vitamin solution. The initial pH of the solution was adjusted to 7.0 using HCl and NaOH. The acid-production chamber, the desalination chamber, and the cathode chamber were filled with 10, 10, and 30 mL of 10 g/L NaCl at the beginning of each batch cycle, respectively. During the start-up operation, the solutions in the chambers were replaced every 24 h. The sampling and data collection operations began after stable voltage outputs were achieved. During the operations, the solutions in all chambers were replaced when the current was <0.5 mA. The period for the solution replacement was defined as a desalination cycle. For each treatment, the sampling and data collection operations were kept for at least three cycles. Four fixed voltages (0.3, 0.6, 0.8, and 1.0 V) were applied to the MEDCC, MEDC, and EDCC circuit using power supplies (Itech, IT6700). For each cell, a resistance (10 \(\Omega\)) was connected between the negative lead of the power supply and the cathode, while the positive lead of the power supply was connected to the anode. Open circuit operations of the MEDCC, MEDC, and EDCC (i.e., the applied voltage = 0 V) under the same conditions were carried out to measure the dialysis effects. As a control experiment to examine the function of microbes, the EDCC was operated with the same conditions as the MEDCC but without microbes in the anode chamber. All experiments were carried out at 30 \(^\circ\)C and conducted at least in duplicate.

#### Analyses and Calculations.
Samples from each chamber were taken at 0, 3, 6, 12, and 18 h in each desalination cycle and used for the following chemical analysis. Concentrations of Cl\(^-\) and PO\(_4\)\(^{3-}\) were determined using ionic chromatography (IC, Metrohm 882). The chemical oxygen demand (COD) was
measured using the dichromate method. Solution conductivities and pH values were measured using a conductivity meter (Leici, DDS-11A) and a pH meter (Leici, PHS-3C), respectively. Output voltages were recorded using a data acquisition system (model 2700, Keithley Instruments, Inc.).

The current density (A/m²) was normalized with the cathode surface area. The Coulombic efficiency (CE) was calculated according to the method of Liu et al. The total salt removal or desalination rate (Dᵢ, %) was calculated by $Dᵢ = (C₀ - Cᵢ)/C₀$ where $C₀$ and $Cᵢ$ are the initial and final conductivities of the solution in the desalination chamber. The acid-production (or alkali-production) efficiency ($η$, %) was calculated as follows:

$η = 100% × \frac{ΔNVF}{Q} = 100% × \frac{ΔNVF}{\sum_{i=1}^{n} Iᵢ}$

Here $ΔN$ is the H⁺ (or OH⁻) concentrations generated in the acid-production (or the alkali-production) chamber based on the changes of pH (M), $V$ is the chamber volume (L), $F$ is Faraday's constant (96,485 C/mol), $Iᵢ$ is the current output (A) at time $tᵢ$ (s), and $Q$ is the recovered coulombs (C).

Statistical significance was evaluated at the level $p < 0.05$.

## RESULTS

### Performances of the MEDCC, MEDC, and EDCC

The performances of the MEDCC were superior to those of the MEDC and the EDCC (Figure 2A). With 1.0 V applied voltage, the maximum current density in the MEDCC (8.4 ± 0.5 A/m²) was about 6 times of that in the EDCC (1.5 ± 0.3 A/m²). Therefore, the microbes in the anode chamber played a critical role on the electrical performance of the MEDCC. The maximum current density of the MEDC (7.7 ± 0.2 A/m²) was about 10% lower than that of the MEDCC, while the time period with high current density in the MEDCC was longer than that in the MEDC. For example, after 18 h, the current density of the MEDC was very low, whereas the current density of the MEDCC was still about 2 A/m². With 0.3–1.0 V applied voltages, the coulombs of the MEDCC were 174–245 C, which were about twice of those of the MEDC (98–120 C). The higher current density with the longer running time in the MEDCC resulted in higher desalination rates. As shown in Figure 2B, at any time, the desalination rates of the MEDCC were higher than those of the MEDC and EDCC. With 10 mL of 10 g/L NaCl, $Dᵢ$ values within 18 h were 86 ± 4%, 60 ± 4%, and 33 ± 2% in the MEDCC, MEDC, and EDCC, respectively.

Higher CE values were achieved in the MEDCC than in the MEDC at different applied voltages (Figure 3). For example, the CE values with the applied voltage of 0.3 V were 62 ± 3% and 32 ± 5% in the MEDCC and MEDC, respectively. With the applied voltage of 1.0 V, the CE values of the MEDCC and MEDC were 97 ± 2% and 65 ± 2%, respectively. As the applied voltages increased from 0 to 1.0 V, the desalination rates of the MEDCC within 18 h increased from 5 ± 1%, which was the desalination rate by dialysis, to 86 ± 2% (Figure 3). The desalination rates of the MEDCC were 23%–26% higher than those of the MEDC with the applied voltages of 0.6–1.0 V.

### pH Change and Cl⁻ Concentrations in the Anode Chamber of the MEDCC and MEDC

With the different applied voltages, pH values of anolyte in the MEDC (or the EDCC) kept near 7.0 throughout the operation time. As shown in Figure 4A, with the applied voltage of 1.0 V, pH values of anolyte in the MEDC decreased from 7.0 to 4.5 within 18 h, while pH values in the MEDCC (or the EDCC) were near 7.0 during the operation time. With the applied voltages of 0–1.0 V, the MEDCC kept the pH values in the anode solution almost the same as the initial value (7.0) (Figure 4B). However, the pH values in the anode solution of the MEDC decreased with the applied voltages: from 7.0 to 5.0 at 0.3 V and from 7.0 to 4.6 at 0.8 V.

The Cl⁻ concentrations in the anode chamber increased to 2.8 g/L in the MEDC within 18 h, while the Cl⁻ concentrations in the anode chamber of the MEDCC remained about 0.8 g/L throughout the operation. Phosphate transferred from the
Acid- and Alkali-Production Performance in the MEDCC. With 1.0 V applied voltage, the pH values (related to acid production) in the acid-production chamber of the MEDCC were lower than those in the EDCC (0.68 ± 0.10 vs 2.2 ± 0.0 in pH unit at 18 h). In the cathode chambers, alkali production of the MEDCC was significantly higher than those of the EDCC (12.9 ± 0.1 vs 12.2 ± 0.2 in pH unit) and the MEDC (12.9 ± 0.1 vs 12.6 ± 0.1 in pH unit) (Figure 5) (*p* < 0.05). Productions of H⁺ and OH⁻ within 18 h from the acid-production chamber and the cathode chamber of the MEDCC were 209 ± 68 and 87 ± 29 mM, respectively, calculated on the basis of the pH values.²¹ However, the H⁺ and OH⁻ productions in the EDCC were only 6 ± 1 and 14 ± 5 mM, respectively. Compared with the EDCC, 35 and 6 times of the H⁺ and OH⁻ productions in the MEDCC showed greatly promising performance of acid- and alkali-production in the cell. On the basis of the cathode chamber volume of 30 mL and the acid-production chamber volume of 10 mL, the total amounts of alkali production and acid production were 2.6 ± 0.9 and 2.1 ± 0.7 mmol, respectively. Calculations using data from different desalination cycles showed that the total amount of alkali production in the MEDCC was about 1.0–1.5 times the acid production in the cell. With the increasing of applied voltages, the pH values in the cathode chamber (in the acid-production chamber) in the MEDCC increased (decreased) (Figure 6A). The acid-production efficiencies in the acid-production chamber increased with the applied voltages, ranging from 29% to 75%. The alkali-production efficiencies were relatively stable (from 90% to 96%) with the applied voltages of 0.3–1.0 V (Figure 6B).

As an additional example to show the MEDCC performance, we also conducted experiments using the MEDCC with deionized water in the acid-production and cathode chambers. In terms of electrical performance, desalination performance, and acid- and alkali-production performance, the results of the MEDCC with 10 g/L NaCl solution in the acid-production and cathode chambers were somewhat better than those of the MEDCC with deionized water in the chambers. However, the results of the MEDCC with deionized water in the chambers were still much better than those of the MEDC and EDCC (see the Supporting Information, Table S1 and Figure S1).

Figure 4. Anolyte pH values in the MEDCC and MEDC (A) changing with time and (B) changing with different applied voltages in 18 h of running time.

Figure 5. pH values in the acid-production and cathode chamber in the MEDCC, EDCC, and MEDC with 1.0 V applied voltage.

Figure 6. Effect of applied voltages on (A) the pH in the acid-production, cathode, and desalination chamber and (B) acid-production and alkali-production efficiencies in 18 h cycles of the MEDCC.
Advantages of the MEDCC. In our study, a novel device (the MEDCC) was developed to desalinate salty water as well as to produce acid and alkali. With applied voltages of 0.3–1.0 V, 62%–97% of CE values were obtained from the MEDCC, which were 1.5–2.0 times the CEs from the MEDC (32%–65%). Considering the differences of the running time, salt concentrations, and volumes of the desalination and anode chambers between previous studies and ours, we converted the desalination percents to desalinated mole numbers per hour for better comparison. In typical batch cycles with an applied voltage of 0.8 V, the desalination rate in the MEDC of Luo et al. was 0.048 mmol/h, whereas the rate reached 0.078 mmol/h in our MEDCC. With 0.6 V applied voltage, the desalination rates within 18 h were 0.072 and 0.043 mmol/h in the MEDCC and the MEDC of Luo et al., respectively, while the desalination rate within 60 h was 0.029 mmol/h in the MEDC of Mehanna et al. with 0.55 V applied voltage. With the commonly applied voltages in the MEDC or MEC, it was demonstrated that the MEDCC had better desalination performance than the MEDC and EDCC.

Such good desalination performance of the MEDCC should be attributed to the favorable electricity generation condition in the MEDCC. The higher applied voltages resulted in higher peak currents and shorter operation periods in the MEDCC, which was consistent with the results of Wang et al. Compared to the MEDC with the similar material and structure (with an applied voltage of 0.55 V) of Mehanna et al., the maximum current density of the MEDCC with 0.6 V applied voltage was about 3 times higher and the CE values were 1–4 times higher. The anode potential in the MEDCC was about −200 mV lower than that in the MEDC, corresponding to the pH values of 7.0 and 4.5, respectively, in the MEDCC and the MEDC. The result was consistent with that of Harnisch et al., in which one unit pH decrease could lead to a change of the anode potential of 59 mV. Although the anodic potential shows a significant effect on the growth of anodic biofilm, there is still no available method to define the optimal anode potential. Our experiments showed that fixing an anode potential of −300 mV in both MEDCC and MEDC did not improve the performance of the cells. Therefore, the good electrical performance in the MEDCC might be a result of the conditions with neutral pH values and without any Cl− accumulation in the anode chamber (Figure 2A). Further research is needed to investigate the effect of anodic potential on the activity of the anodic biofilms.

Comparison of the Acid- and Alkali-Production Efficiencies. The different efficiencies of acid production and alkali production were attributable to the different mechanisms of the two production processes in the MEDCC. The O2− production in the MEDCC was based on the reaction of O2+2H2O+4e−→4OH−, in which O2 accepted e− easily with the high redox potential in the cathode chamber. Therefore, the current efficiency with alkali production was relatively stable at 90%−96%. However, the amount of acid production was dependent on the efficiency of the water dissociation reaction with the BPM, while the efficiency of the water dissociation process was positively correlated to the current density in the MEDCC. Harnisch et al. demonstrated that a low current flow was not a result of the water dissociation reaction but from the leakage current, i.e., the diffusion of the electrolyte solution into the BPM and the subsequent migration of the respective ions through the AEM and CEM layers. In our experiments, the maximum current density was 0.84 mA/cm2 using 10 g/L NaCl solution in the acid and cathode chambers. The result suggested that the low H+ production was attributable to the low current density in the MEDCC. Moreover, according to Bauer et al., the current efficiency of the acid-production was a function of the current density. As the current density decreased from 10 to 0 mA/cm2, the efficiency decreased rapidly from 75% to 0%. Our data also supported such a relationship. It was notable that compared with the results reported by Heijne et al., the BPM in our study worked very well, partly because of the higher current density achieved (0.84 mA/cm2 in this study vs 0.45 mA/cm2 in the literature).

The H+ leakage through the AEM is another limiting factor of the acid-production. In the MEDCC, the H+ leakage resulted in the pH decrease in the desalination chamber. With the applied voltage of 0.3 V, the pH values changed from 6.9 ± 0.1 to 1.5 ± 0.1 within 18 h. The H+ leakage caused about 16% of acid-production efficiency loss. However, the acid production efficiency was about 60% lower than the alkali production efficiency with the applied voltage of 0.3 V. The result indicated that the low efficiency of water dissociation with the BPM at low current density was the more critical factor for the low acid production efficiency than the H+ leakage through the AEM.

As a novel system, the MEDCC can be further improved. For example, research is needed to prevent the H+ leakage in the acid-production chamber and to control the pH values in the desalination chamber by improving the AEM using some novel materials. The mechanism of ion transfer processes in the MEDCC is under investigation. It should be noticed that the salt concentrations in the acid and alkali solutions were pretty high, which would reduce the potential use of the products. The problem resulted from the NaCl solutions added in the acid-production and cathode chambers in the current experiments.

Outlook. According to the Global Water Intelligence prediction, the global desalination capacity will reach 97.5 million m3/d by 2015, indicating a 140% annual increase over a 10-year period. Water desalination requires about 1.05 × 1013 kWh/yr electrical power in the future. In terms of costs, electrodialysis is competitive with the other technologies for salty water with salinity between 0.4 and 6 g/L. We demonstrate that the MEDCC should be potentially a better solution to desalinate salty water than electrodialysis, as it will use less energy and generate the additional economic benefit of acid and alkali byproducts.

On the basis of the works of Rabaey et al. and Logan et al., we can estimate the potential economic benefit of the byproducts from the MEDCC. The alkali production is used as an example. With 1.0 V applied voltage within 18 h, the MEDCC can produce 0.10 g of NaOH with 7.46 × 10−3 kWh electricity. In other words, to produce NaOH in the MEDCC, the energy input is 0.71 kWh/kg NaOH and the cost is about $0.07. The market price of NaOH is seven times higher than the cost. Nevertheless, with such a small-scale reactor, the cost-effective analysis is still preliminary.

ASSOCIATED CONTENT

Supporting Information
One additional figure and one table. This material is available free of charge via the Internet at http://pubs.acs.org.
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