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Electrochemical Desalination Using Bi/BiOCl Electrodialysis Cells

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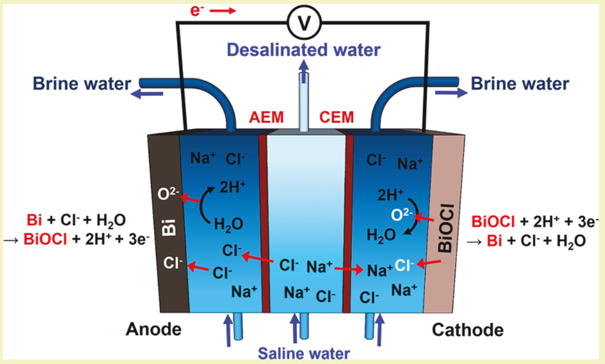
ABSTRACT: The construction of new types of electrodialysis (ED) cells composed of Bi and BiOCl electrodes were investigated to achieve more cost-effective desalination using ED. By using the oxidation of Bi to BiOCl and the reduction of BiOCl to Bi as the anode and cathode reactions, respectively, the Bi/BiOCl ED cells decreased the equilibrium cell voltage to 0 V. As a result, the operating voltage of the Bi/BiOCl ED cells could be significantly lowered compared with the current ED cells. Two-compartment and three-compartment ED cells were constructed and their configurations and operating principles were explained in detail. The electrochemical and desalination performances of these cells containing different electrolytes were analyzed to examine the effects of the cell configuration and pH of the electrolytes on the operating voltage as well as Cl^- and Na^+ removal efficiencies. The results and discussion provided in this study will enable further development of Bi/BiOCl ED cells for use in desalination, wastewater treatment, and Cl^- removal applications.



KEYWORDS: *Bi electrode, BiOCl electrode, Cl-storage electrode, Cl ion removal, Na ion removal, Deionization, Wastewater treatment*

INTRODUCTION

Currently, about two-thirds of the world's population lives in areas of water stress where the demand for fresh water exceeds the supply of fresh water for at least one month of the year.[1] This clearly demonstrates that lack of access to fresh water is a serious global issue.[2−4] Developing cost-effective desalination methods to increase access to fresh water is imperative.[1,5−7] While conventional desalination methods such as distillation and reverse osmosis (RO) are based on physical processes,[6−10] various desalination technologies based on electrochemical processes have been recently reported,[11−24] providing new approaches to manage energy, water, and salts.

Electrodialysis (ED), which can remove salt ions from saline water under the influence of an electric voltage, is one of the most established electrochemical desalination methods.[25−29] Unlike distillation or RO where water molecules are removed from saline water, ED removes salt ions from saline water. Since the amount of salt is significantly less than the amount of water, even in seawater (∼3.5 wt % NaCl), ED has the potential to achieve desalination with a higher recovery of feedwater at a lower cost than other desalination methods. However, currently, ED is cost-effective only for brackish water desalination.[10] This is because the electrical energy input required for ED increases as the salt concentration increases. Thus, current ED cells cannot compete with RO for seawater desalination.

Typical ED cells utilize water reduction to H_2 as the cathode reaction and Cl^- oxidation to Cl_2 or water oxidation to O_2 as the anode reaction.[10,29] The simplest ED cell configuration, which is composed of a cathode compartment, an anode compartment, and a middle compartment containing saline water to be desalinated, is shown in Figure 1. The cathode compartment and the middle compartment are divided by a cation exchange membrane (CEM) while the anode compartment and the middle compartment are divided by an anion exchange membrane (AEM). When a voltage is applied, cations in the middle compartment move toward the cathode compartment where cations are consumed (e.g., H^+) and anions move toward the anode compartment where anions are consumed (e.g., Cl^-) to maintain charge neutrality in each

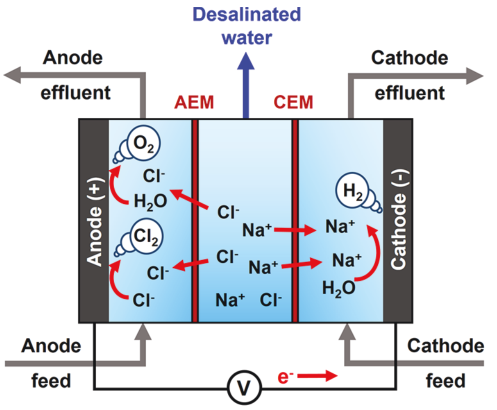


Figure 1. Scheme for desalination performed by a conventional ED cell.

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compartment. As a result, desalination is achieved in the middle compartment.

The overall voltage required to operate an ED cell (V_{OP}) can be calculated using eq 1. $E^e_{cathode}$ and E^e_{anode} represent the equilibrium potentials for the cathode and anode reactions, $\eta_{cathode}$ and η_{anode} represent the overpotentials for the cathode and anode reactions, and V_{loss} is the voltage loss in the cell. This voltage loss can be caused by solution resistance or junction potentials across the membranes. $E^e_{cathode} - E^e_{anode}$ is the equilibrium cell voltage (V^e_{cell}) when current flow is negligible and it is determined by the choice of cathode and anode reactions as well as the electrolyte composition. The signs of V_{OP} and V^e_{cell} for ED cells are negative, which means that an electrical energy input is required for operation. However, in this study, the negative signs will be omitted and magnitudes will be discussed for convenience

$$V_{OP} = E^e_{cathode} - E^e_{anode} - \eta_{cathode} - \eta_{anode} - V_{loss} \tag{1}$$

$$V^e_{cell} = E^e_{cathode} - E^e_{anode} \tag{2}$$

The V^e_{cell} of an ED cell that performs water reduction at the cathode and water oxidation at the anode is 1.23 V while that of an ED cell that performs water reduction at the cathode and Cl^- oxidation at the anode is 1.36 V under standard conditions. Identifying cathode and anode reactions that can be used in an ED cell with a smaller V^e_{cell} is one straightforward method to lower the V_{OP} and overall operating cost of an ED cell.

Recently, we have discovered that Bi can serve as an effective and practical Cl-storage electrode.[18] Bi can store and release Cl^- by the reversible conversion between Bi and BiOCl. We demonstrated that when Bi as a Cl-storage electrode was coupled with $NaTi_2(PO_4)_3$ as a Na-storage electrode, a high capacity desalination battery could be constructed where energy storage and desalination were achieved simultaneously.[18]

In the present study, we investigated the possibility of constructing ED cells using Bi and BiOCl electrodes, which can achieve desalination without the use of a Na-storage electrode. The Bi/BiOCl ED cells use the forward and reverse reactions of the same reaction (i.e., the conversion between Bi and BiOCl) as the anode and cathode reactions, respectively. This means that the V^e_{cell} will be negligible, thus providing a strategy to considerably lower the V_{OP} for ED operation. The operating principles, construction, and desalination performances of Bi/BiOCl ED cells with various configurations are reported.

EXPERIMENTAL SECTION

Materials. NaCl (99%, Sigma-Aldrich), $BiCl_3$ (≥98%, Sigma-Aldrich), HCl (37%, Sigma-Aldrich) and Polyethylene glycol (PEG) (Molecular weight of 6000, USB Corporation) were used without further purification. Deionized water (Barnstead E-pure water purification system, resistivity >18 MΩ cm) was used to prepare all solutions.

Synthesis of Bi and BiOCl Electrodes. The Bi electrodes used in this study were prepared by electrodeposition using a previously reported method.[18] An undivided two-electrode cell was used with a Ti sheet as the cathode and a Pt sheet as the anode. The exposed areas of the Ti and Pt electrodes were 7 cm^2 and 5 cm^2, respectively. An aqueous solution containing 14 mM $BiCl_3$, 1.4 M HCl, and 2.5 g/L PEG 6000 was used as the plating solution. Galvanostatic deposition was performed at 6 A for 1 min using a dc power supply (TP3010E, Tekpower), resulting in the deposition of Bi ($Bi^{3+} + 3e^- \rightarrow Bi$, $E° = 0.286$ V vs SHE) on the Ti cathode. The average voltage between the Ti cathode and Pt anode was ∼7.5 V. In this process, water reduction to H_2 occurred concurrently with the Bi deposition. The H_2 bubbles that formed during the deposition served as an in situ template to create a foam structure.[30] During the deposition, the solution was stirred at 300 rpm. After deposition, the Bi electrodes were rinsed with water and dried in air. The BiOCl electrodes used in this study were prepared by electrochemically oxidizing Bi electrodes in an undivided three-electrode cell composed of a Bi working electrode (WE), a Pt counter electrode (CE), and a Ag/AgCl (4 M KCl) reference electrode (RE). The Pt electrode was prepared by sputter coating a 100 nm thick Pt layer over a 20 nm thick Ti adhesion layer onto a clean glass slide (LGA Thin Films). A 0.6 M NaCl solution was used as the electrolyte and a potential of 0.5 V was applied versus the RE until the anodic current decreased to zero. The X-ray diffraction patterns and scanning electron microscopy images of as-deposited Bi films and BiOCl films obtained after chlorination and electrochemical properties and cyclability of Bi and BiOCl electrodes can be found in our previous report.[18]

Electrochemical Characterization. Before constructing ED cells, half-cell performances of the Bi and BiOCl electrodes were first examined in an undivided three-electrode cell. In these experiments, a Bi or BiOCl electrode was used as the WE with a Pt CE and a Ag/AgCl (4 M KCl) RE. The change of the electrode potential was recorded while applying a constant current of ±1 mA cm^{-2} (anodic current for the Bi electrode and cathodic current for the BiOCl electrode). 60 mM NaCl (pH 6) or 65 mM HCl (pH 1.2) was used as the electrolyte. The electrolyte was unstirred during electrochemical testing.

ED Cell Construction and Performance Testing. For electrodialysis tests, a custom-built multicompartment Teflon cell was used. Ion-exchange membranes could be inserted between the compartments as desired. Various two- and three-compartment cells were constructed, and detailed cell configurations are described in the Results and Discussion section. For two-compartment cells, a CEM (Nafion 117, Fumatech) was used as the divider. For three-compartment cells, an AEM (PEEK, Fumatech) was used in addition to the CEM (Nafion 117, Fumatech). The electrolyte volume of all three compartments was 10 mL. The area of the AEM and CEM exposed to the electrolyte was 5.7 cm^2. The distance between the Bi and BiOCl electrodes was 1.6 cm for the two-compartment cell and 3.2 cm for the three-compartment cell. The desalination performances of the ED cells were investigated while operating the cells galvanostatically at 1 mA cm^{-2}. Applying a higher current density may increase the probability of a side reaction occurring at the cathode (i.e., H_2 evolution). Therefore, for accurate measurements of salt removal efficiency and pH changes caused only by the cell reactions, 1 mA cm^{-2} was chosen for cell operation in this study.

The solutions in all compartments of the ED cells were not circulated or stirred. The potentials of Bi and BiOCl electrodes against a Ag/AgCl (4 M KCl) RE were monitored so that potential changes of the individual electrodes as well as the V_{OP} could be recorded. The operating voltage applied between the Bi and BiOCl electrodes could be found by taking the difference between the potential applied to the cathode against the RE and the potential applied to the anode against the RE. The Ag/AgCl RE was immersed in the Bi compartment near the Bi electrode for all experiments.

The Cl^- concentration of the desalination compartment (Bi compartment for the two-compartment cell and middle compartment for the three-compartment cell) was measured using a chloride ion meter (Horiba 6560−10C) after passing 20 C. Before the measurement, 0.1 M KNO_3 was dissolved in the solutions as a supporting electrolyte and the pH was adjusted to 9 with KOH. This condition provided optimum solution conductivity and pH for the operation of the chloride ion-selective electrode of the chloride ion meter. The Na^+ concentration in the desalination compartment and pH of all compartments were measured after passing a charge of 0, 5, 10, 15, or 20 C using a sodium ion meter (Horiba B-722) and a pH meter (Fisher scientific AB15), respectively. The experimentally measured Cl^- and Na^+ concentrations were compared with theoretically

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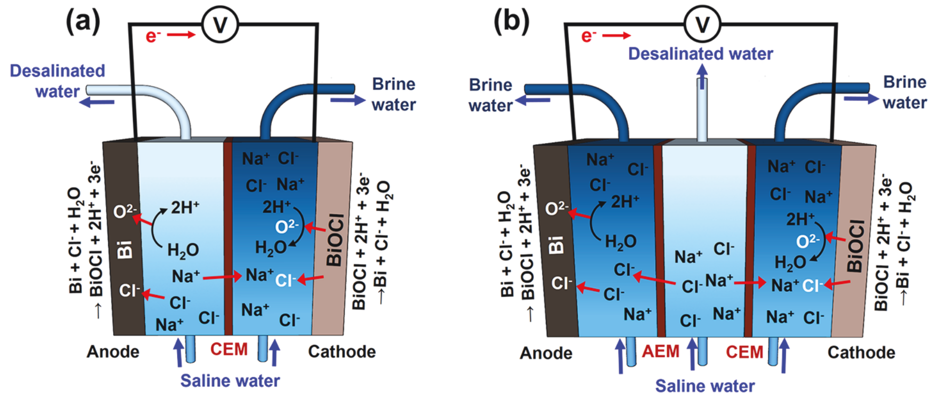

Figure 2. Cell configurations and operating schemes of (a) two- and (b) three-compartment Bi/BiOCl ED cells for desalination.

expected Cl^- and Na^+ concentrations based on the charge passed during electrodialysis tests. The moles of Cl^- and Na^+ removed during electrodialysis were calculated using the following equations:

$$\text{mol of Na}^+ \text{ removed for all cell types} = \text{mol of electrons passed during electrodialysis} \quad (3)$$

$$\text{mol of Cl}^- \text{removed for two-compartment cell} = \frac{\text{mol of electrons passed during electrodialysis}}{3} \quad (4)$$

$$\text{mol of Cl}^- \text{removed for three-compartment cell} = \text{mol of electrons passed during electrodialysis} \quad (5)$$

RESULTS AND DISCUSSION

Configuration and Operating Principles of the Bi/BiOCl ED Cells. The Bi/BiOCl ED cell uses Bi as the anode and BiOCl as the cathode. The anode reaction is the oxidation of Bi to BiOCl (eq 6) and the cathode reaction is the reduction of BiOCl to Bi (eq 7).

$$\text{Bi} + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{BiOCl} + 2\text{H}^+ + 3e^- \quad E^\circ = 0.160 \text{ V vs SHE} \quad (6)$$

$$\text{BiOCl} + 2\text{H}^+ + 3e^- \rightarrow \text{Bi} + \text{Cl}^- + \text{H}_2\text{O} \quad E^\circ = 0.160 \text{ V vs SHE} \quad (7)$$

By using the forward and reverse of the same reaction as the anode and cathode reactions in the same electrolyte, the V^e_{cell} is lowered to 0 V. Therefore, only the $\eta_{cathode}$, η_{anode}, and V_{loss} contribute to the V_{OP} of the ED cell, which can significantly decrease the electrical energy consumption required for desalination. Furthermore, since the oxidation of Bi to BiOCl occurs at a much more negative potential (E° = 0.160 V vs SHE) than the oxidation of Cl^- (E° = 1.36 V vs SHE), this ED cell effectively suppresses the formation of chlorine gas at the anode. In typical ED cells Cl^- oxidation is used as the major anode reaction or occurs as a side reaction, which can cause serious corrosion and safety problems.[28]

In this study, both two-compartment and three-compartment Bi/BiOCl ED cells were constructed and their desalination performances were comparatively investigated. In the two-compartment cell (Figure 2a), the cathode and anode compartments both contained 60 mM NaCl to mimic brackish water and were separated by a CEM. When a voltage is applied, the Bi anode is oxidized to BiOCl by consuming Cl^- and the BiOCl cathode is reduced to Bi, causing Cl^- to be released (eqs 6-7). For every Cl^- ion that is consumed during the conversion of Bi to BiOCl, three electrons move from the Bi anode to the BiOCl cathode. This electron movement is coupled with the movement of three Na^+ ions from the Bi compartment to the BiOCl compartment through the CEM to maintain charge neutrality in both compartments. Since Cl^- are stored by the Bi anode and Na^+ move toward the BiOCl compartment, desalination is achieved in the Bi compartment while brine water is generated in the BiOCl compartment. Ideally, removal of one Cl^- ion and three Na^+ ions is expected per movement of three electrons from the anode to the cathode. When Bi is completely converted to BiOCl and BiOCl is completely converted to Bi, the two electrodes can be swapped to continue the desalination/salination processes.

The three-compartment cell contains an additional (middle) compartment between the Bi and BiOCl compartments (Figure 2b). The middle compartment and the Bi compartment are divided by an AEM, while the middle compartment and the BiOCl compartment are divided by a CEM. During the conversion of Bi to BiOCl, three electrons move from the Bi anode to the BiOCl cathode. The movement of these electrons is coupled with the movement of three Cl^- ions from the middle compartment to the Bi compartment and three Na^+ ions from the middle compartment to the BiOCl compartment to maintain charge neutrality in all compartments. Thus, desalination is achieved in the middle compartment and brine water is generated in both the Bi and BiOCl compartments.

The main difference between the two cells is that the three-compartment cell can remove three Na^+ ions and three Cl^- ions per three electrons, while the two-compartment cell can remove three Na^+ ions and one Cl^- ion per three electrons. Therefore, the three-compartment cell is expected to remove more salt ions than the two-compartment cell when the same amount of charge has been passed. However, the V_{loss} is expected to be smaller in the two-compartment cell because there is a shorter distance between the two electrodes and one less membrane present in the cell. Another difference between the two cells is related to specificity for ion removal. In the three-compartment cell, there is no specificity for ion removal (any cations or anions present in solution will be removed to maintain charge neutrality), but the two-compartment cell is specific for Cl^- removal, although it is not specific for cation removal. Therefore, for applications that require the selective removal of Cl^- (e.g., wastewater treatment), the two-compartment cell may be more effective. The different Bi/

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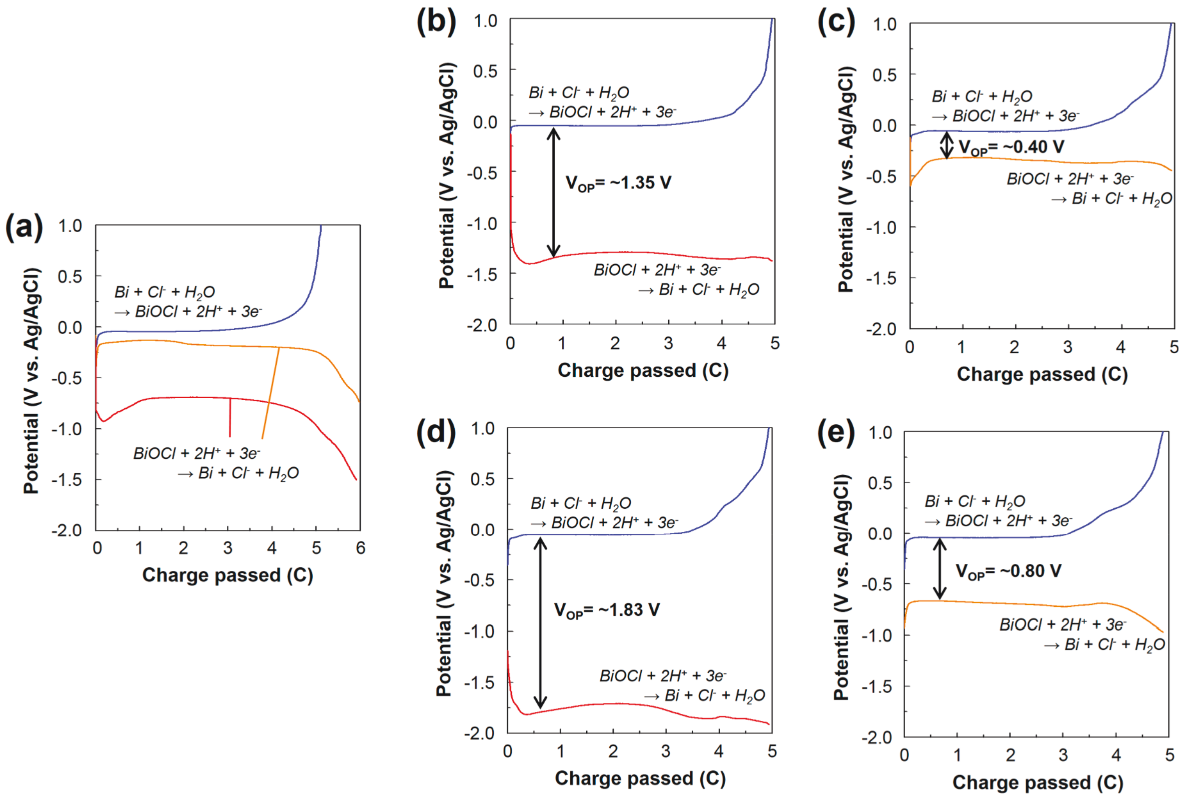

Figure 3. Potential−charge plots for Bi and BiOCl electrodes measured vs a Ag/AgCl RE at ±1 mA cm^{-2} obtained (a) in an undivided cell as half-cell reactions, (b) in a two-compartment Bi(60 mM NaCl)/BiOCl(60 mM NaCl) cell, (c) in a two-compartment Bi(60 mM NaCl)/BiOCl(65 mM HCl) cell, (d) in a three-compartment Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl) cell, and (e) in a three-compartment Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl) cell.

BiOCl ED cell configurations thus provide more flexibility for using these cells for various applications.

Half-Cell Tests of the Bi/BiOCl Electrodes. Before constructing the ED cells described above, half-cell tests of the Bi and BiOCl electrodes were first performed to examine the individual performances of the electrodes. The electrolyte used was 60 mM NaCl (pH 6) to mimic brackish water. To test the Bi electrode, an undivided three-electrode cell composed of a Bi WE, a Pt CE, and a Ag/AgCl RE was used.

The blue line in Figure 3a shows the potential change of the Bi electrode against the RE when the oxidation reaction of Bi to BiOCl was performed galvanostatically at a rate of 1 mA cm^{-2}. Upon initiation of the oxidation reaction, the potential of Bi rapidly increased from its open circuit potential (−0.38 V) to ca. −0.04 V vs Ag/AgCl and plateaued until the reaction was terminated, which is indicated by a sharp increase of the potential above 1.0 V.

The performance of the BiOCl electrode was examined in the same three-electrode cell composed of a BiOCl WE, a Pt CE, and a Ag/AgCl RE. The red line in Figure 3a shows the potential change of the BiOCl electrode against the RE when the reduction of BiOCl to Bi was performed at a rate of −1 mA cm^{-2}. When the reduction initiated, the potential of the BiOCl electrode decreased rapidly from its open circuit potential (−0.13 V vs Ag/AgCl) and plateaued at ca. −0.69 V vs Ag/AgCl.

The equilibrium potential of the Bi/BiOCl redox reaction in 60 mM NaCl (pH 6) solution is −0.0523 V vs SHE (equivalent to −0.25 V vs Ag/AgCl), which is calculated using the Nernst equation. When this value is compared to the experimental values reported above, the overpotential required by the BiOCl electrode to form Bi was calculated to be ~0.44 V, which is much greater than the overpotential required by the Bi electrode to form BiOCl (~0.21 V). This means that the reduction kinetics of BiOCl to Bi are much more sluggish than the oxidation kinetics of Bi to BiOCl, which was also reported in the previous study.[18]

In our previous study, it was demonstrated that the kinetics for BiOCl reduction could be improved significantly in acidic media.[18] Therefore, we also investigated the performance of the BiOCl electrode using a 65 mM HCl solution (pH 1.2) as the electrolyte and a rate of −1 mA cm^{-2}, as above (orange line in Figure 3a). Using an acidic solution, the potential of the plateau for the dechlorination of BiOCl to Bi was ~0.18 V vs Ag/AgCl. Since the equilibrium potential for the reduction of BiOCl to Bi in a 65 mM HCl solution (pH 1.2) is −0.061 V vs Ag/AgCl, the overpotential required for the BiOCl reduction under this condition was only ~0.12 V.

On the basis of these results, two-compartment Bi/BiOCl cells were constructed with two electrolyte configurations. One cell contained 60 mM NaCl in both the Bi and BiOCl compartments, which is denoted as Bi(60 mM NaCl)/BiOCl(60 mM NaCl). The other cell contained 60 mM NaCl in the Bi compartment and 65 mM HCl in the BiOCl compartment, which is denoted as Bi(60 mM NaCl)/BiOCl(65 mM HCl).

The potential−charge plots for the Bi(60 mM NaCl)/BiOCl(60 mM NaCl) cell operated at 1 mA cm^{-2} are shown in Figure 3b. In this cell, a Ag/AgCl RE was added in the Bi compartment to monitor the individual electrode potentials

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(both the cathode and anode) against the Ag/AgCl RE in addition to the V_{OP}. The difference between the potentials applied to the Bi and BiOCl electrodes against the Ag/AgCl RE represents the V_{OP} of the cell required to achieve a current density of 1 mA cm^{-2}, which was measured to be ~1.35 V for this cell. Since the Ag/AgCl RE was located in the Bi compartment, the potential profile of the Bi electrode shown in Figure 3b is very similar to that obtained for the half-cell reaction of Bi shown in Figure 3a. However, the potential profile of the BiOCl electrode shown in Figure 3b was shifted to the negative direction compared with that of the half-cell reaction shown in Figure 3a. This is because additional potential had to be applied to the BiOCl electrode to compensate for the voltage loss in solution due to the greater distance between the RE and BiOCl electrode and the presence of the CEM to achieve 1 mA cm^2. In other words, the difference between the potential profiles of BiOCl shown in Figure 3a,b is due to the V_{loss} in solution of the ED cell.

Figure 3c shows the potential-charge plots for the Bi(60 mM NaCl)/BiOCl(65 mM HCl) cell. In this case, the V_{OP} of the cell operated at 1 mA cm^{-2} was significantly reduced from ~1.35 to ~0.40 V. This is mainly due to a decrease in overpotential required for the dechlorination of the BiOCl electrode in 65 mM HCl although a shift in the $E^{\circ}_{cathode}$ to the positive direction in this solution (by 0.19 V) also made a contribution.

We also constructed three-compartment Bi/BiOCl cells with two different electrolyte configurations. One cell contained 60 mM NaCl in all three compartments, which is denoted as Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl). In the other cell, the 60 mM NaCl in the BiOCl compartment was replaced with 65 mM HCl and is denoted as Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl).

The potential-charge plots of the Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl) cell operated at 1 mA cm^{-2} are shown in Figure 3d. Again, a Ag/AgCl RE was placed in the Bi compartment to monitor the changes of the potentials applied to the cathode and anode as well as the V_{OP} during ED operation. Compared with the two-compartment cell operating under the same conditions, the V_{OP} was much greater (~1.83 V). This is because the V_{loss} in solution was increased by the increase in the distance between the electrodes as well as by the addition of another membrane. This change was manifested as a negative shift of the BiOCl electrode potential versus the RE.

Figure 3e shows the potential−charge plots of the Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl) cell operated at 1 mA cm^{-2}. The use of an acidic solution again resulted in a decrease in the V_{OP} from ~1.83 V to ~0.80 V, primarily due to a decrease in overpotential required for the reduction of the BiOCl electrode.

The results shown in Figure 3a−e are encouraging because the V_{OP}s of the Bi/BiOCl ED cells, which include V^{e}_{cell}, $\eta_{cathode}$, η_{anode}, and V_{loss} are comparable or smaller than the V^{e}_{cell} of conventional ED cells using H_2 production/Cl_2 production (1.36 V) or H_2 production/O_2 production (1.23 V) before other voltage requirements are taken into account.

Desalination Performance of the Bi/BiOCl Cells. The desalination performances of the various Bi/BiOCl ED cells were investigated by examining the change in Na^+ and Cl^- concentrations in the desalination compartment of each cell. Unless otherwise specified, the ED cells were operated at 1 mA cm^{-2} and 20 C of charge was passed.

The changes in Cl^- concentration were measured using a chloride ion meter and are summarized in Table 1. For the two-compartment cells, where one Cl^- ion should be removed per three electrons, the concentration of Cl^- is expected to decrease from 60 to 53.09 mM in the Bi compartment after passing 20 C. Since removal of Cl^- in this compartment is achieved by direct uptake of Cl^- by the Bi electrode to form BiOCl and there are no possible competing oxidation reactions that can occur at the potential used for the conversion of Bi to BiOCl,[18] 100% Faradaic efficiency was expected. Indeed, the decrease in the Cl^- concentration in the Bi compartment after passing 20 C was very close to the expected value for both the Bi(60 mM NaCl)/BiOCl(60 mM NaCl) and Bi(60 mM NaCl)/BiOCl(65 mM HCl) cells (Table 1).

Table 1. Theoretically Expected and Observed Changes in the Cl^- Concentration in the Desalination Compartments of the Four ED cells after Passing 20 C[a]

cell configuration	theoretically expected Cl^- concentration (mM)	experimentally measured Cl^- concentration (mM)
Two-Compartment Cell		
Bi(60 mM NaCl)/BiOCl(60 mM NaCl)	53.1	53.6
Bi(60 mM NaCl)/BiOCl (65 mM HCl)	53.1	53.1
Three-Compartment Cell		
Bi(60 mM NaCl)/60 mM NaCl/ BiOCl (60 mM NaCl)	39.3	39.2
Bi(60 mM NaCl)/60 mM NaCl/ BiOCl (65 mM HCl)	39.3	38.4

[a]Bi compartment of the two-compartment cells and the middle compartment of the three-compartment cells.

For the three-compartment cells where three Cl^- ions should be removed per three electrons, the concentration of Cl^- is expected to decrease from 60 mM to 39.27 mM in the middle compartment after passing 20 C. Unlike the two-compartment cells which specifically remove Cl^- in the Bi compartment, Cl^- removal in the middle compartment of the three-compartment cells is not Cl-specific: Any anion can move through the AEM to maintain charge neutrality. However, since the concentration of OH^- is negligible at pH 6, and Cl^- is the only other anion available in the middle compartment, the amounts of Cl^- removed from the middle compartment of both the Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl) and Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl) cells were very close to the theoretically expected values.

The changes in Na^+ concentration were measured using a sodium ion meter. The removal of Na^+ cannot be predicted as easily as the removal of Cl^- because both H^+ and Na^+ can move through the CEM. The movement of H^+ is expected to interfere with the movement of Na^+ when the pH of the Bi compartment decreases significantly as the conversion of Bi to BiOCl progresses (eq 6) or when 65 mM HCl is used in the BiOCl compartment. Therefore, the removal of Na^+ needs to be examined carefully in conjunction with the pH changes of all compartments. We measured the change in Na^+ concentration in the desalination compartment and the change in pH in all compartments after passing 5, 10, 15, and 20 C in each of the four cells operated at 1 mA cm^{-2}. The results are summarized in Table 2.

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Table 2. Theoretically Expected and Observed Changes in Na^+ Concentration in the Desalination Compartment of the Four ED Cells[a]

cell configuration	5 C	10 C	15 C	20 C
theoretically expected Na^+ concentration	54.8 mM	49.6 mM	44.4 mM	39.2 mM
Two-Compartment Cell				
Bi(60 mM NaCl)/BiOCl(60 mM NaCl)	54.5 mM (105.8%)	49.5 mM (101.0%)	46.9 mM (84.0%)	44.1 mM (76.4%)
Bi(60 mM NaCl)/BiOCl(65 mM HCl)	50.2 mM (188.5%)	43.3 mM (160.6%)	36.6 mM (150.0%)	30.9 mM (140.0%)
Three-Compartment Cell				
Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl)	54.7 mM (101.9%)	49.8 mM (98.1%)	45.1 mM (95.5%)	39.5 mM (98.6%)
Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl)	48.9 mM (213.5%)	43.1 mM (162.5%)	36.0 mM (153.9%)	33.7 mM (126.4%)

[a]The Na^+ removal efficiency is shown in parentheses.

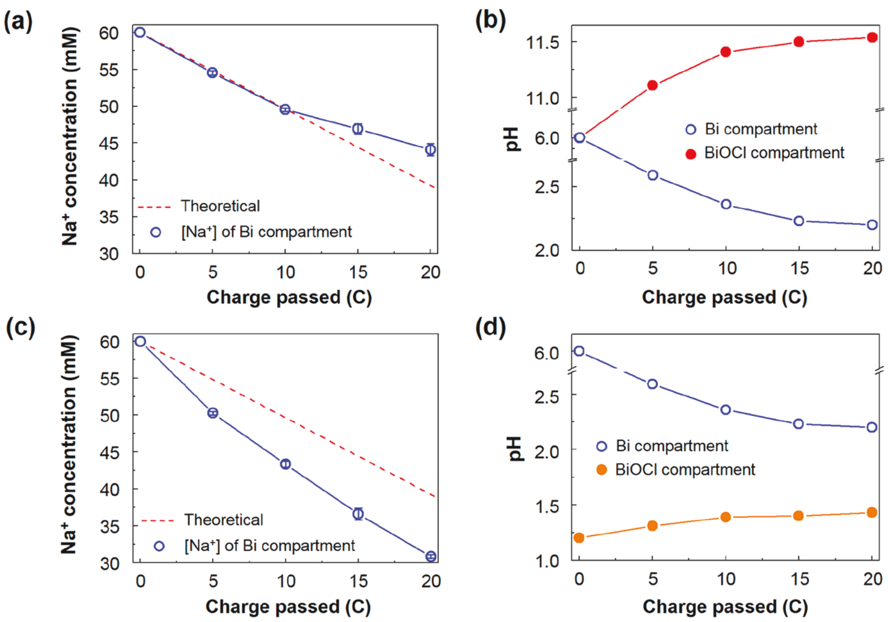

Figure 4. (a) Change in Na^+ concentration in the Bi compartment and (b) change in pH in Bi and BiOCl compartments of the Bi(60 mM NaCl)/BiOCl(60 mM NaCl) cell operated at 1 mA cm^{-2}; (c) change in Na^+ concentration in the Bi compartment and (b) change in pH in Bi and BiOCl compartments of the Bi(60 mM NaCl)/BiOCl(65 mM HCl) cell operated at 1 mA cm^{-2}.

Figure 4a shows the theoretically expected (dotted lines) and observed (circles) changes in Na^+ concentration in the Bi compartment of the two-compartment Bi(60 mM NaCl)/BiOCl(60 mM NaCl) cell. The result shows that up to 10 C the concentration of Na^+ decreases as expected because the concentration of H^+ in the Bi compartment initially containing 60 mM NaCl is negligible. However, beyond this point, the pH of the Bi compartment decreased below 2.5 as a result of the generation of H^+ during the oxidation of Bi to BiOCl (eq 6). As a result, H^+ as well as Na^+ could move through the CEM, decreasing the amount of Na^+ removed. The Na^+ removal efficiency can be represented by the ratio of the experimentally observed amount of Na^+ removed to the theoretically expected amount of Na^+ removed:

$$\text{Na}^+ \text{ removal efficiency (\%)} = \frac{\text{observed amount of Na removed}}{\text{expected amount of Na removed}} \times 100\% \quad (8)$$

The Na^+ removal efficiency of this cell after passing 20 C was calculated to be 76.7%. This means that on average 2.3 Na^+ ions and 0.7 H^+ ions (instead of 3 Na^+ ions) were removed per 3 electrons passed in the Bi compartment.

For the two-compartment Bi(60 mM NaCl)/BiOCl(65 mM HCl) cell, a Na^+ removal efficiency greater than 100% (Figure 4c) was observed. This is due to the initial concentration differences of Na^+ and H^+ in the Bi and BiOCl compartments, which results in the exchange of Na^+ and H^+ by diffusion. (Na^+ moves to the BiOCl compartment and H^+ moves to the Bi compartment.) This diffusion-driven exchange of Na^+ and H^+ occurs in addition to the electron-coupled cation movement that occurs during the cell operation, resulting in a calculated Na^+ removal efficiency greater than 100%. The Na^+ removal efficiency was the highest at the beginning of the cell operation since this is when the Na^+ and H^+ concentrations of the Bi(60 mM NaCl) and BiOCl(65 mM HCl) compartments differ the most and when the greatest amount of cation diffusion occurs. As more charge was passed, the pH in the Bi compartment gradually decreased (eq 6), while the pH in the BiOCl compartment gradually increased (eq 7; Figure 4d). As a result, the diffusion-driven cation exchange slowed down and the Na^+ removal efficiency decreased. For example, the Na^+ removal efficiency at 5 C passed was 188.29% which decreased to 140.55% at 20 C passed. This result means that after passing 20 C, on average, 4.2 Na^+ ions were removed from and 1.2 H^+ ions were added to the Bi compartment per three electrons passed.

The three-compartment Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl) cell showed a ~100% Na^+ removal efficiency throughout the cell operation (Figure 5a), meaning

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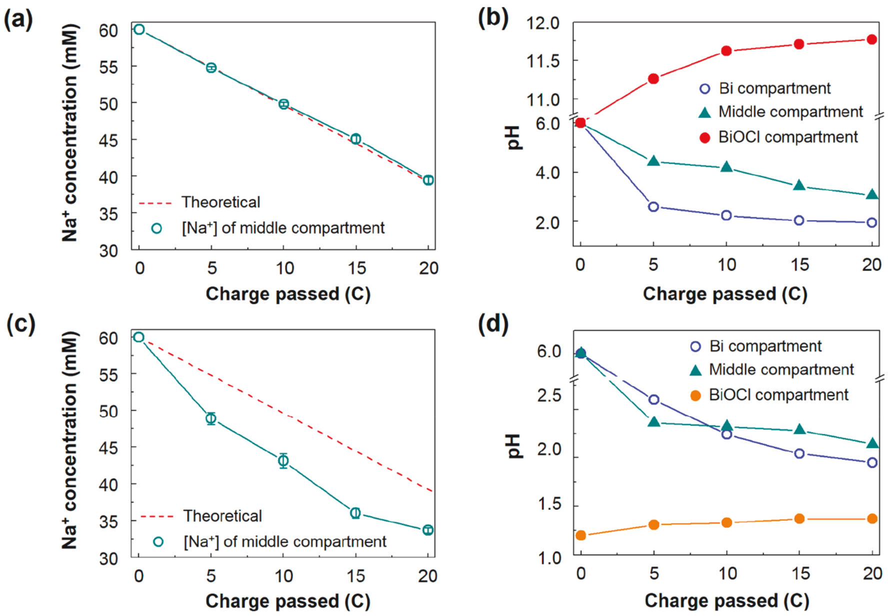

Figure 5. (a) Change in Na^+ concentration in the middle compartment and (b) change in pH in all compartments of the Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl) cell operated at 1 mA cm^{-2}; (c) change in Na^+ concentration in the middle compartment and (d) change in pH in all compartments of the Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl) cell operated at 1 mA cm^{-2}.

that three Na^+ ions were removed in the middle compartment per three electrons passed as expected. This is because the pH of the middle compartment remained above 3, so the concentration of H^+ remained negligible in the middle compartment during ED cell operation. Ideally, the pH of the middle compartment should be near 6 because the H^+ generated in the Bi compartment should not pass through the AEM. However, Figure 5b shows a slight pH decrease in the middle compartment, suggesting that a trace amount of H^+ (1 mM of H^+ after 20 C passed) diffused from the Bi compartment to the middle compartment through the AEM due to its imperfect impermeability to H^+.

The three-compartment Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl) cell showed a Na^+ removal efficiency greater than 100% for the same reason explained above for the two-compartment Bi(60 mM NaCl)/BiOCl(65 mM HCl) cell. The Na^+ removal efficiency was the highest (214.91%) after passing 5 C because the differences in Na^+ and H^+ concentrations between the middle and BiOCl compartments was the greatest at the beginning of ED operation, leading to fast diffusion-driven Na^+—H^+ exchange. As ED cell operation progressed, the pH of the BiOCl compartment gradually increased, and the pH of the middle compartment decreased (Figure 5d), which caused the diffusion-driven movement of Na^+ and H^+ to slow. After passing 20 C, the Na^+ removal efficiency decreased to 127%. This means that on average 3.8 Na^+ ions were removed from and 0.8 H^+ ions were added to the middle compartment per 3 electrons passed. We note that although the Na^+ removal efficiency varied between the four ED cells, all cells showed an excellent Na^+ removal efficiency between 77 and 140% after a charge of 20 C was passed.

■ CONCLUSION

In summary, we constructed new types of ED cells based on Bi/BiOCl electrodes which utilize the reversible conversion of Bi and BiOCl as the anode and cathode reactions. This results in an equilibrium cell voltage of 0 V, which significantly reduces the overall operating voltage and therefore the operating cost of the ED cells reported here. The configuration and operating principles of two- and three-compartment cells were explained, and their advantages and the disadvantages were examined and compared. Since the kinetics of the cathode reaction (conversion of BiOCl to Bi) could be significantly improved by lowering the pH, the two- and three-compartment cells were constructed with the BiOCl compartment containing both 60 mM NaCl and 65 mM HCl, resulting in the construction of four different ED cells: Bi(60 mM NaCl)/BiOCl(60 mM NaCl), Bi(60 mM NaCl)/BiOCl(65 mM HCl), Bi(60 mM NaCl)/60 mM NaCl/BiOCl(60 mM NaCl), and Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl). The V_{OP} for these cells operated galvanostatically at 1 mA cm^{-2} were ∼1.35, ∼0.4, ∼1.83, and ∼0.8 V, respectively. This clearly demonstrates the advantage of replacing the 60 mM NaCl solution with 65 mM HCl in the BiOCl compartment, which is a decrease in the V_{OP} by ∼1 V. The Cl^- and Na^+ removal efficiencies of the desalination compartments were systematically investigated in conjunction with the pH changes of all compartments in each of the four cells. The three-compartment cell, Bi(60 mM NaCl)/60 mM NaCl/BiOCl(65 mM HCl), achieved the highest NaCl removal efficiency. We note that the ED cells used in this study were batch-type cells where the electrolyte was stagnant during the ED cell operation. We expect that the V_{OP} can be further decreased by constructing a flow-type cell where the electrolyte flow and electrode geometry/configurations are optimized. The construction of Bi/BiOCl cells with four different configurations and analysis of their performances provided in this study will serve as a good foundation to further improve Bi/BiOCl ED cells for desalination, wastewater treatment, and Cl-removal applications.

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The authors declare no competing financial interest.

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