Evaluation of recovery characteristic of acidic and alkaline solutions from NaNO₃ using conventional electrodialysis and electrodialysis with bipolar membranes

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Abstract–We compared the electrodialysis performance for HNO_3 and NaOH recovery from $NaNO_3$ solution by conventional electrodialysis (ED) and electrodialysis with bipolar membranes (EDBM) at constant current and constant voltage. The individual resistances of the components of the electrodialysis systems were also evaluated. The electrodialysis extent for HNO_3 and NaOH recovery from $NaNO_3$ solution was almost proportional to the total amount of electricity supplied to the system, regardless of the operation mode and the electrodialysis systems. For the same volume of feed solution, the energy consumption and current efficiency differed depending on the operation mode and the electrodialysis system. In both the ED and EDBM systems, the conductivity of the feed solution strongly affected the overall cell resistance after approximately 50% of the ions in the feed solution had migrated.

Key words: Electrodialysis, Acid, Base, Bipolar Membrane (BM), Cation Exchange Membrane (CEM), Anion Exchange Membrane (AEM)

INTRODUCTION

In many industrial chemical processes, a variety of salt solutions, which are mixtures of organic and inorganic acids and bases, are present in the discharge streams. The recovery and reuse of acid and base solutions from salt solutions before discharge are important for improving the environmental friendliness of these processes. This concept has been applied in a carbonate-based process to treat waste uranium oxide mixtures [1-7]. In this process, uranium is selectively dissolved in sodium carbonate solution containing hydrogen peroxide to form a uranyl peroxocarbonate complex ion, $UO_2(O_2)(CO_3)_2^{4-}$, after which the dissolved uranyl peroxocarbonate complex solution is acidified to precipitate UO_4 from the solution, with CO_2 gas being released from the solution. HNO_3 and NaOH solutions are required for the acidification and recovery of sodium carbonate solution and can be recovered from the supernatant solution after UO_4 precipitation by electrodialysis [1,3,6,7].

Electrodialysis (ED) has been widely used to separate or concentrate ionic species from salt solutions using a variety of combinations of homopolar membranes, such as cation-exchange membranes (CEM) and anion-exchange membranes (AEM), or bipolar membranes (BM) arranged in parallel according to their intended function [1,8-12]. Bipolar membranes are composed of a cation-exchange layer joined back-to-back to an anion-exchange layer with an intermediate junction between them. Water splitting occurs at the boundary between the anion and cation layers under reverse bias, generating hydroxyl ions at the anodic side and proton ions at the cathodic side [7,9,11-15].

Two types of electrodialysis systems can be used to recover acid and base solutions from the waste salt solutions [1,8-10,16,17]. The

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first is a conventional ED cell arrangement consisting of repeating a set of CEM and AEM in series placed between the cathode and anode, as shown in Fig. 1(a), which illustrates the recovery of HNO_3 and NaOH from $NaNO_3$ solution. The second is electrodialysis with bipolar membrane (EDBM) cell arrangement, which consists of repeating a set of BM, CEM, AEM, and BM with the cathode and anode placed only at the ends of the membrane stack, as shown in Fig. 1(b).

The conventional ED and EDBM systems have advantages and disadvantages. In conventional ED, anodes and cathodes are repeatedly placed at the end of every AEM and CEM pair. In contrast, in EDBM, only one anode and one cathode are used, placed at the ends of the total membrane configuration, which saves space in the electrodialysis unit and results in a lower initial construction cost than that of conventional ED. In conventional ED, the acidity or alkalinity of the solutions in contact with the electrode increases during the operation because of increases in the amount of protons or hydroxyl ions generated at the electrode surfaces due to water-splitting, which accelerates the electrode surface deterioration, especially the dissolution of the anode in strongly acidic conditions. In contrast, in EDBM, the solutions between the electrode and bipolar membrane can be kept constant as an initial condition, because for every hydroxyl ion (proton) generated at the electrode, a proton (hydroxyl ion) is generated at the bipolar membrane surface to maintain the neutrality of the solution, which can preserve the membrane and electrode integrities over longer periods. Additionally, there are no byproducts from unnecessary electrode reactions. Despite the advantages of using bipolar membranes, however, the bipolar membrane is much more expensive than the anion- and cation-exchange membranes, and water-swelling could occur at the intermediate boundary in bipolar membranes, requiring EDBM systems to be operated more carefully than conventional ED systems.

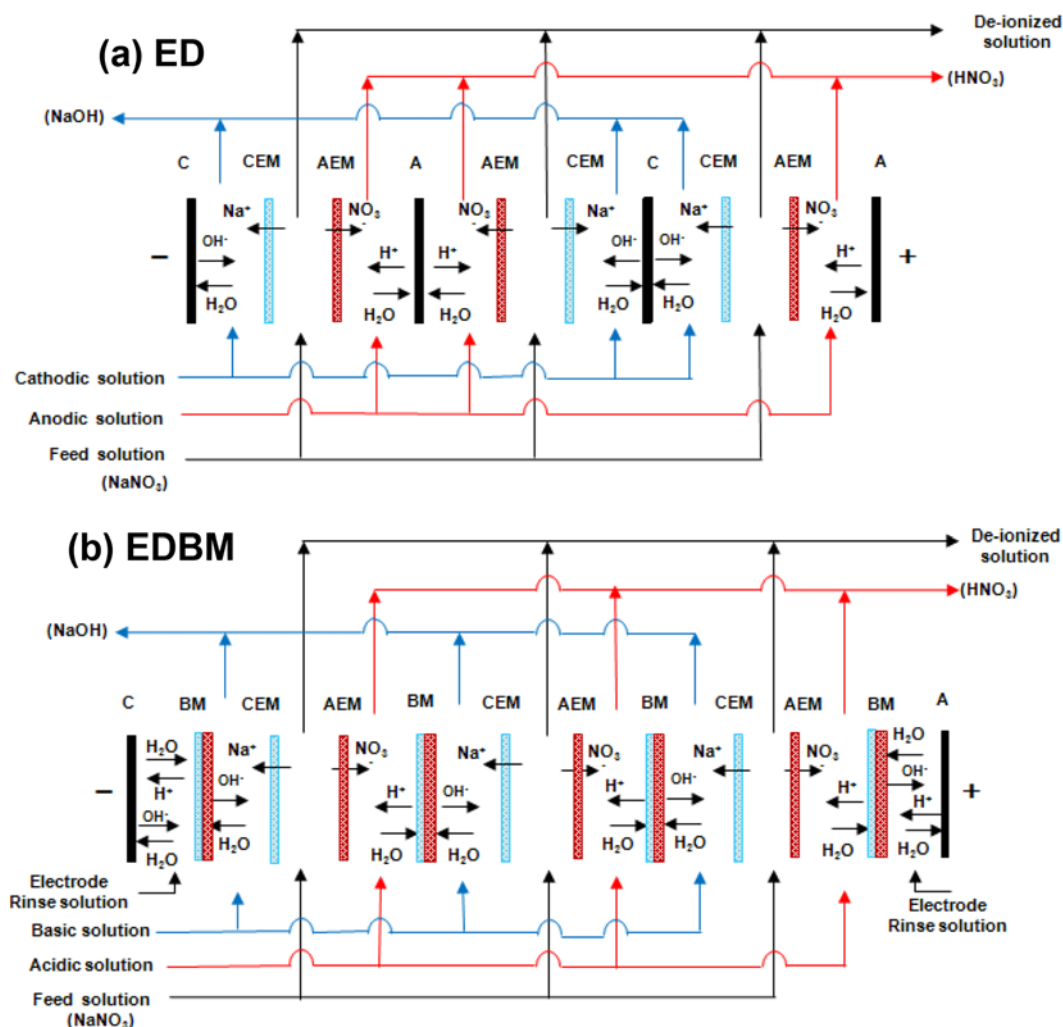To date, a direct comparison of electrodialysis performance to

Fig. 1. Cell configurations of conventional electrodialysis ((a) ED) and electrodialysis with bipolar membranes ((b) EDBM) for the recovery of acid and base solutions from a salt solution (C: cathode, A: anode, CEM: cation exchange membrane, AEM: anion exchange membrane, BM: bipolar membrane).

recover acid and base solutions from a salt solution is hindered by a lack of data. In this work, the use of conventional ED and EDBP to recover HNO_3 and NaOH from a $NaNO_3$ salt solution was studied by varying several variables in a batch setup and comparing their performances in terms of current efficiency and energy consumption. Then, the resistance of each component of the electrodialysis systems was analyzed during electrolysis.

EXPERIMENTAL

To compare the performance of conventional ED and EDBP systems for recovering acid and base solutions from a salt solution, two laboratory-scale electrodialysis systems, with one repeating configuration unit using electrodes and membranes based on Fig. 1, were prepared for batch operation. The cell configuration for the conventional ED was cathode-CEM-AEM-anode, featuring cathodic, feed, and anodic compartments. In the cathodic compartment of a conventional ED system, a base solution is concentrated by cation migration from the feed solution through the CEM and the generation of hydroxyl ions due to water splitting at the cathode. In the

anodic compartment of a conventional ED system, an acid solution is concentrated by the migration of anions from the feed solution through the AEM and the generation of protons due to water splitting at the anode. The EDBP cell configuration was cathode-BM-CEM-AEM-BM-anode and included a cathode rinse compartment, a basic compartment, a feed compartment, an acidic compartment, and an anode rinse compartment. In the basic compartment of the EDBP system, a base solution is concentrated by the migration of cations from the feed solution through the CEM and the generation of hydroxyl ions due to water splitting at the bipolar membrane. In the acidic compartment of the EDBP system, an acid solution is concentrated by the migration of anions from the feed solution through the AEM and the generation of protons due to water splitting at the bipolar membrane. In the cathode and anode rinse compartments, the hydroxyl ions and protons generated at the cathode and anode are offset by the protons and hydroxyl ions generated at the bipolar membranes, respectively, keeping the initial electrode rinse solutions constant during the operation.

A cation exchange membrane (ASTOM, Neosepta CMX-SB) and an anion exchange membrane (ASTOM, Neosepta AMX-SB) were

used for ED and EDBM. A bipolar membrane (ASTOM, Neo-septa BP-E) was used only for the EDBM system. The membranes were used as received, without any pretreatment, after being stored in demineralized water. Each compartment was formed by frames with a 3.5×8×0.7 cm vacant space (approximately 30 ml). All cell parts were made of polyethylene. Silicon gaskets of 0.5 mm were placed between the frames and membranes. In the electrodialysis systems, the anode (cathode) was an IrO₂-coated Ti electrode (Ti electrode) with dimensions of 2×4×0.1 cm and a 6 mm×3 mm mesh.

For the batch experiments using the electrodialysis systems, a basic solution with an initial concentration of 0.1 M NaOH, an acidic solution with an initial concentration of 0.1 M HNO₃, and a 0.5 M NaNO₃ feed solution were circulated through the cathodic compartment, anodic compartment, and feed compartment, respectively, and their 250 ml volumetric flask reservoirs by peristaltic pumps. In the EDBM system, a 0.1 M NaOH electrode rinse solution was circulated through the cathode and anode rinse compartments and its volumetric flask reservoir. The volume of each circulating solution was 200 ml. To control the experimental temperature in the batch experiments, the electrodialysis system was placed in a glass port filled with water that was circulated into a chiller set at 25±1 °C. A constant voltage or current was supplied to the electrodialysis systems by a poten-tiostat/galvanostat (Wonatec, WMPG1000). In all experiments, the pH and conductivity of the circulating solutions were recorded online by pH-meters and conductivity-meters, respectively, and a data-log-ger (Almemo 5990-2) controlled by a computer. During the elec-trodialysis experiments, each electrolyte solution was sampled at

regular intervals to analyze the concentrations of NO₃⁻ and OH⁻ or Na⁺ ions with an auto-titrator or ion chromatography (Dionex, ICS 90).

All of the chemicals used in this work were reagent grade and were dissolved as received in 18.2 MΩ demineralized water pre-pared by double distillation and an ion-exchanger (Milli-Q Plus).

RESULTS AND DISCUSSION

1. Evaluation of Values of Several Variables Measured During Electrodialysis in the Systems

To compare the HNO₃ and NaOH recovery from NaNO₃ solu-tion by the ED and EDBM systems, as shown in Figs. 2 to 5, the NaNO₃, NaOH, and HNO₃ concentrations (a), cell voltages or cell currents (b), pH (c), and conductivity (d) were measured in the feed reservoir, basic reservoir (for the cathodic compartment of the ED system or the basic compartment of the EDBM system), and anodic reservoir (for the anodic compartment of the ED system or the acidic compartment of the EDBM system) as a function of time in batch operation for constant-voltage (12, 15, and 18 V) and constant-cur-rent (40, 60, and 100 mA/cm²) electrodialysis. In those experiments, an initial feed solution of 0.5 M NaNO₃, an initial basic solution of 0.1 M NaOH (for the cathodic compartment of the ED system or the basic compartment of the EDBM system) and an initial anodic solution of 0.1 M HNO₃ (for the anodic compartment of the ED system or the acidic compartment of the EDBM system) were cir-culated within the compartments and their respective reservoirs.
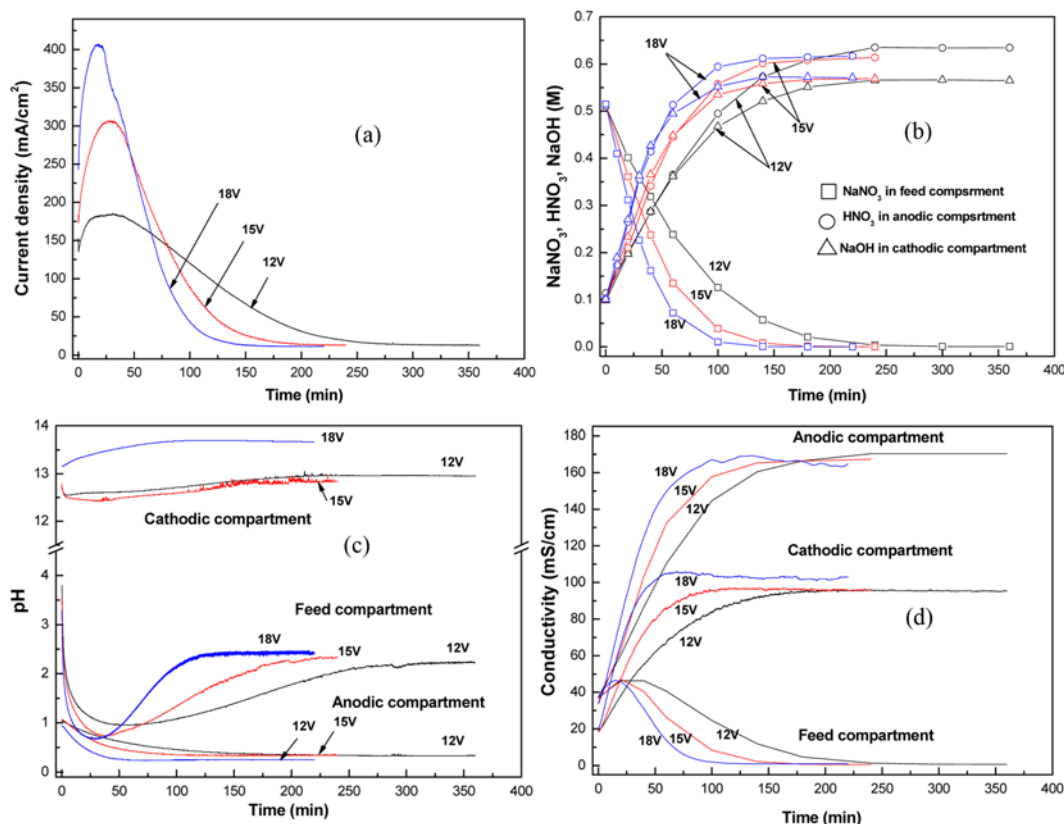

Fig. 2. Changes in the current density (a), concentrations (b), pHs (c), and conductivities (d) in the feed, cathodic, and anodic solutions with electrodialysis time at constant voltages of 12, 15, and 18 V in the conventional ED system.
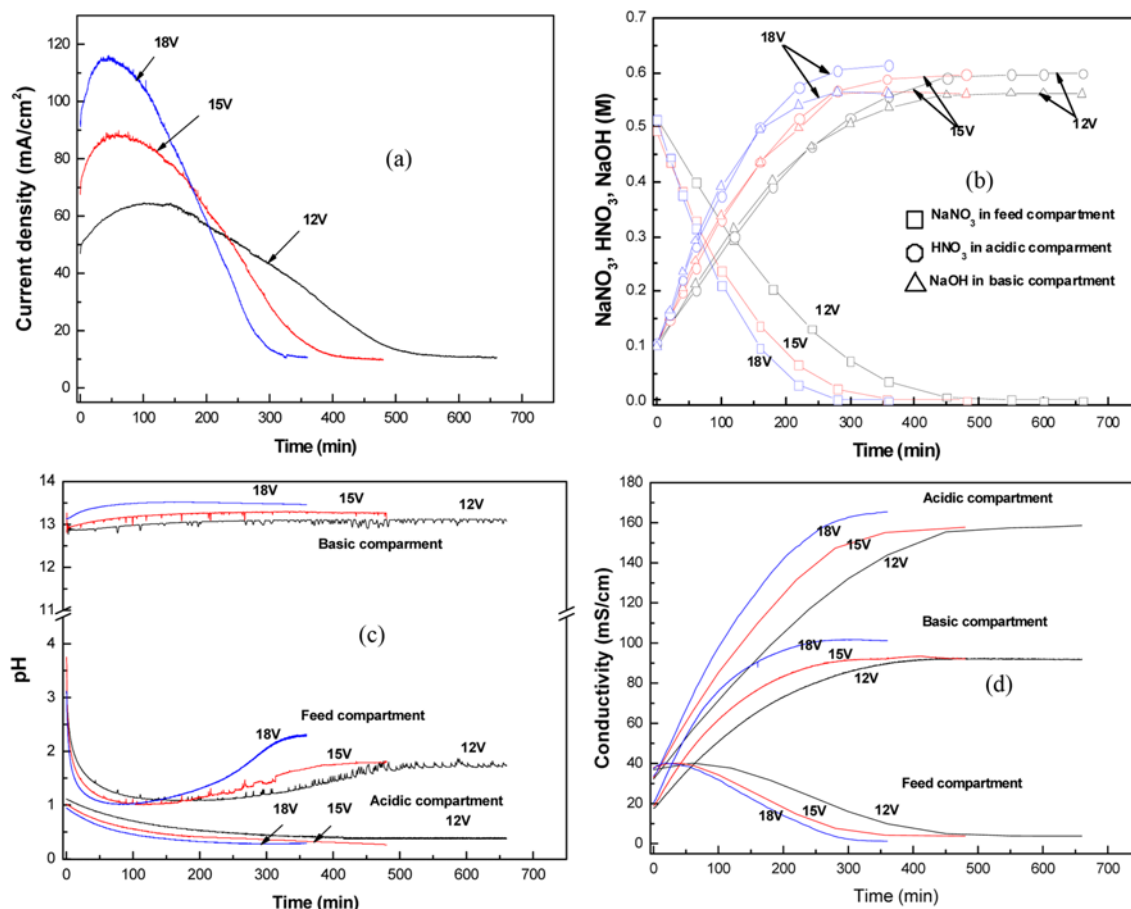
Fig. 3. Changes in the current density (a), concentrations (b), pHs (c), and conductivities (d) in the feed, cathodic, and anodic solutions with electrodialysis time at constant voltages of 12, 15, and 18 V in the EDBM system.

For the EDBM system, an initial solution of 0.1 M NaOH was circulated through both the cathode rinse and anode rinse compartments. The electrode rinse solution flowing between the electrodes and the bipolar membranes facing the electrodes was not affected by the ions migrating through the ion exchange membranes during electrodialysis. Therefore, the concentration, conductivity and pH of the electrode rinse solution remained constant throughout the electrodialysis. These values are not plotted in Figs. 3 and 5 to avoid cluttering the figures.

Figs. 2 and 3 show the results of the constant-voltage operation mode at 12, 15, and 18 V in the conventional ED and EDBM systems, respectively. The overall patterns were similar for both systems, but the current peaks and their amplitudes were sharper and higher, respectively, in the conventional ED system than in the EDBM system. The concentration, pH, and conductivity in each compartment of the conventional ED system changed more rapidly than those in the EDBM system. Because the $NaNO_3$ in the feed initially decreased linearly as a function of time, the concentration of HNO_3 in the anodic compartment of the ED system and the acidic compartment of the EDBM system and the concentration of NaOH in the cathodic compartment of the ED system and the basic compartment of the EDBM system increased almost linearly as well. They then approached their steady-state values. The NO_3^- and Na^+ migration rates increased with increasing applied cell voltage. A small

deviation in the concentrations of recovered NaOH was observed in the figures. This deviation was ascribed to the difference in the amounts of transferred water from the feed solution to the cathodic and anodic sides due to electrolytic osmosis during the electrodialysis. Approximately 10% of the feed water transferred to the concentrated solution sides through the CEM and AEM due to electrolytic osmosis, and approximately 3% more of the feed water transferred to the cathodic side, across the CEM, than to the anodic side, across the AEM. Considering the water transfer, the decrease in the $NaNO_3$ in the feed solution was almost the same as the increase of NO_3^- and Na^+ in each compartment. At the same applied voltage, the cell current in the EDBM system is lower than that of ED system because the EDBM system has a higher cell resistance due to the two bipolar membranes and two electrode rinse compartments present in the EDBM system but not the ED system. This difference in cell resistance makes the ED system faster than the EDBM system. The current peaks occurred when approximately 50% of the ions in the feed solution had migrated under the applied voltages. Under constant-voltage operation, the current is reversely proportional to the overall cell resistance through the electrodialyzer. Accordingly, the current peaks must occur at the lowest cell resistance during the electrodialysis. As the electrodialysis began, the conductivities in the cathodic compartment of the ED system or the basic compartment of the EDBM system increased because of

the generation of NaOH. Similarly, the conductivities in the anodic compartment of the ED system or the acidic compartment of the EDBM system increased because of the generation of HNO₃. The conductivity behavior in the feed compartments was very similar to that of the measured current, indicating that the overall cell resistance during the electrodialysis strongly depends on the feed solution conductivity. As the ions in the feed solution were exhausted, the rate of the drop in conductivity for the feed compartment decreased, which resulted in the rapid increase of the overall cell resistance even though the other compartments had higher-conductivity solutions due to their higher concentrations of HNO₃ and NaOH. This phenomenon will be discussed in more detail in Fig. 9 and the corresponding text.

One interesting feature of Figs. 2 and 3 is the pH behavior of the feed solution during electrodialysis. The pH of the feed solution dropped rapidly as soon as the electrodialysis began and then decreased gradually. However, it increased again when the current began to decrease rapidly. If the Na^+ and NO_3^- ions in the feed solution migrate equally across the cation and anion exchange membranes, respectively, the pH in the feed solution should remain constant during the electrodialysis. The decrease in the pH of the feed solution in the beginning is ascribed to the difference in the number of ions transported across the anion and cation exchange membranes. It is known that the transport rates of anions can be affected by the ion form such as monoatomic anion and polyatomic anions and their affinities to membranes [18]. The lowest pH in the feed solution occurred at a similar time to the current peaks. The pH in

the solution was observed to re-rise again after the times of current peaks. The re-rise in the feed solution pH is considered to be attributed to some of the OH^- ions in the cathodic compartment (or the basic compartment) being strongly attracted toward the anode side under the large potential gradient that existed between the electrodes as the $NaNO_3$ in the feed solution is almost electrodialyzed [1]. This potential gradient causes the back-transfer of OH^- ions into the feed compartment, even across the cation exchange membrane, which slows the migration of Na^+ ions in the feed compartment into the cathodic compartment (or the basic compartment) and also affects the total energy consumption during the electrodialysis. The increase in the pH in the ED system was slightly higher than that in the EDBM system.

Figs. 4 and 5 show the results of the constant-current operation at 40, 60, and 100 mA/cm² in the conventional ED and EDBM systems, respectively. The overall trends are similar for both systems, just like the constant-voltage results. The behavior of the ion concentrations and conductivities was different from those in the constant-voltage operation. The electrodialysis rate increased almost linearly with the current used in each constant-current operation. At the same applied current, the electrodialysis rates in the ED and EDBM system were almost identical. The concentrations varied almost linearly, exhibiting a slight slowing with time, as did the conductivities. As the Na^+ and NO_3^- ions in feed compartment are migrated through the CEM and AEM, only the conductivity in the feed solution decreased and the cell voltage increased. This means that the feed solution strongly affected the overall cell resistance
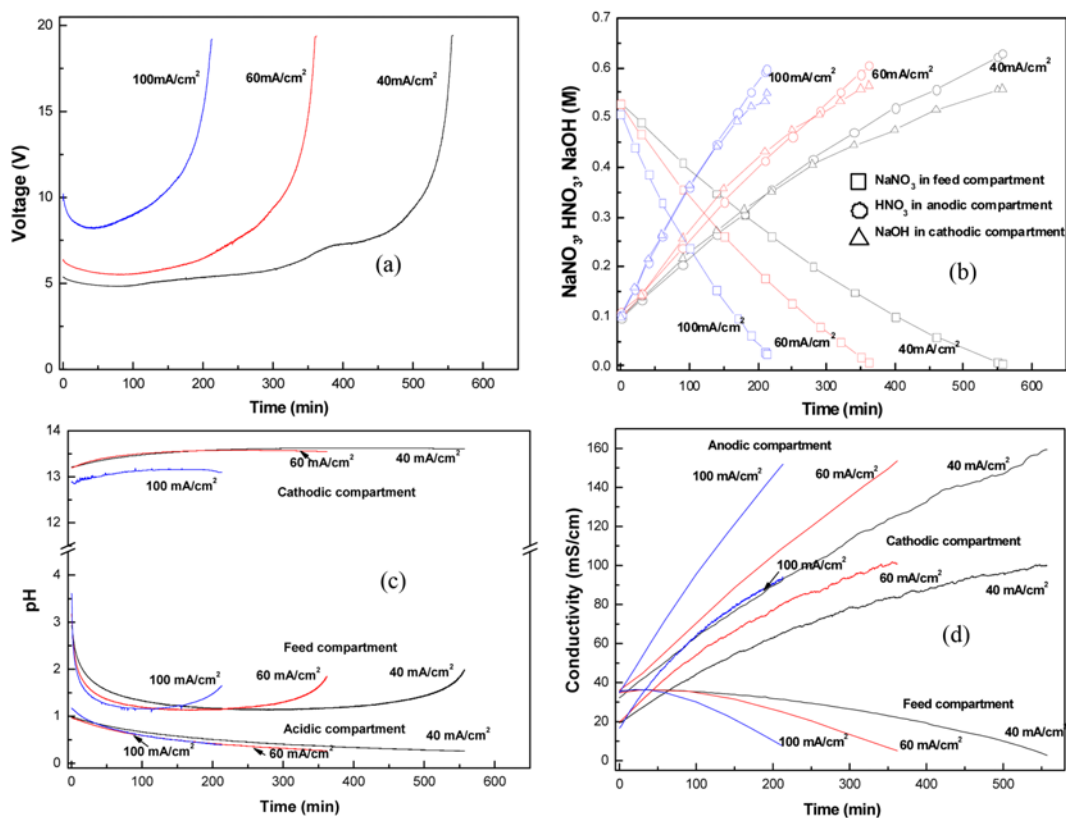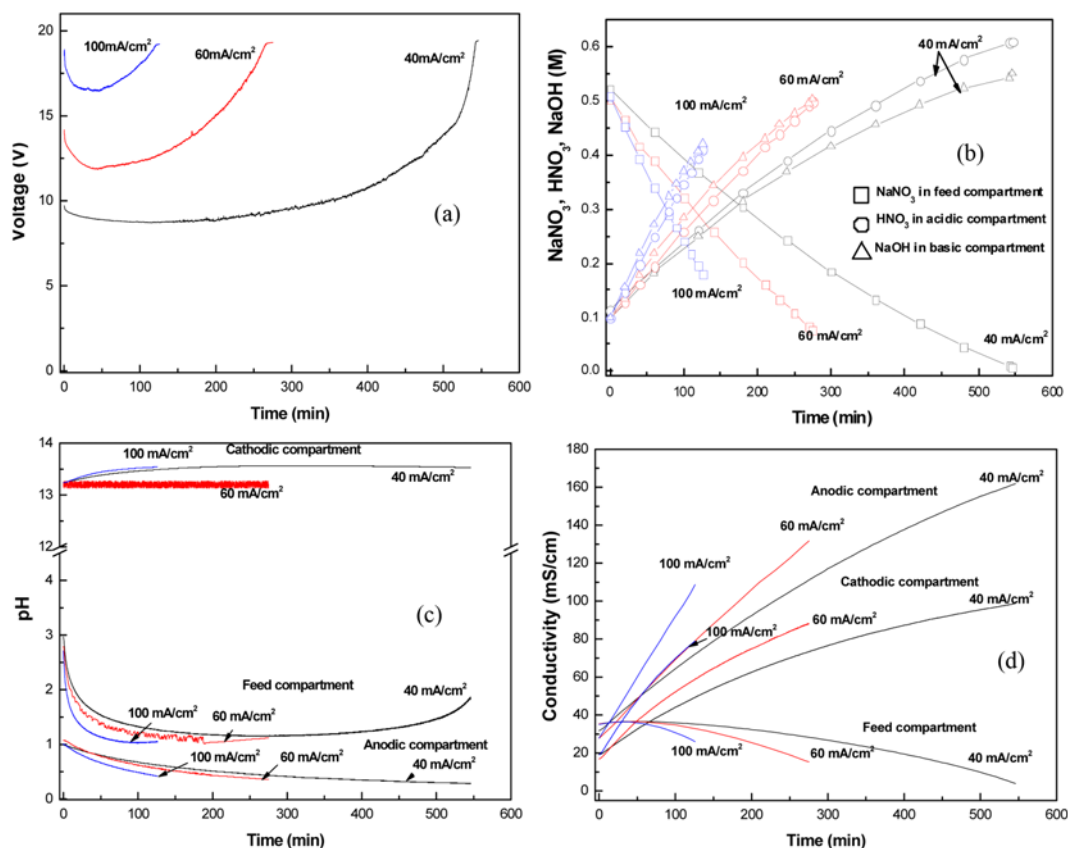

Fig. 4. Changes in the cell voltage (a), concentrations (b), pHs (c), and conductivities (d) in the feed, cathodic, and anodic solutions with electrodialysis time at constant currents of 40, 60, and 100 mA/cm² in the conventional ED system.

Fig. 5. Changes in the cell voltage (a), concentrations (b), pHs (c), and conductivities (d) in the feed, cathodic, and anodic solutions with electrodialysis time at constant currents of 40, 60, and 100 mA/cm^2 in the EDBP system.

during the electrolysis. When approximately 80% of the feed ions were electrodialyzed (when the NaNO$_3$ concentration in the feed solution reached approximately 0.1 M), the cell voltage began to abruptly increase, eventually reaching the voltage compliance limit of 20 V of the power supply used in the work, causing electrodialysis breakoff. To treat the same amount of feed solution, the cell voltage of the EDBM system is larger than that of ED system because additional voltage drops due to the bipolar membranes and the electrode rinse compartments affect the overall cell voltage of the EDBM system. This difference in increasing rate of cell voltage caused the electrodialysis breakoff to occur earlier in the EDBM system. Thus, the electrodialysis for HNO$_3$ and NaOH recovery from NaNO$_3$ could not be completely accomplished. The pH re-rise in the feed solution approximately after the time at which the cell voltage was minimum was observed in both ED and EDBM in constant-current operation, just as it did for the constant-voltage operation described above. This increase occurred at approximately the same time as the rapid increase in the cell voltage.

2. Comparison of Performance Characteristics in the Electrodialysis Systems

Fig. 6 shows the relationship between the electrodialyzed yield of NaNO$_3$ in the feed solution and the total electricity supplied in the ED and EDBM systems under constant-voltage (a) and constant-current (b) operations, which were calculated from the results in Figs. 2 to 5. The plots of the electrodialyzed yield of NaNO$_3$ in the feed vs. the total supplied electricity during the electrodialysis

showed good linearity, with regression coefficients of approximately 0.99. Thus, the electrodialysis recovery of HNO$_3$ and NaOH from NaNO$_3$ solution is almost proportional to the total amount of electricity supplied to the system, regardless of the operation mode, and the electrolysis systems. Fig. 7 shows the energy consumption in the conventional ED and EDBM systems as a function of electrodialyzed NaNO$_3$ yield in the feed solution under constant-voltage (a) and constant-current (b) operation, which were calculated using the results in Figs. 2 to 5. Under constant-voltage operation, higher applied voltages consumed more energy to electrodialyze the same amount of feed solution, and the electrodialysis rate increased with voltage. At the same applied voltage, the energy consumption of the EDBM system was slightly lower than that of the ED system for the same volume of feed solution because the cell current in the EDBM system was lower than that in the ED system, even though the EDBM electrodialysis rate was lower than that of the ED system, as shown in Figs. 2 and 3. The cause of this difference is likely to be the lower pH re-rise phenomena, as shown in Figs. 2 and 3, which corresponds to less back-attraction of OH$^-$ ions in the basic compartment into the feed compartment. Another contribution to this phenomenon is that, for a given amount of electricity supplied in the electrodializer, a lower current flow through the electrodialyzer causes less side reaction of water split at the electrodes, giving more sufficient electrodialysis equilibrium condition in the system, which leads to lower energy consumption. In the constant-current operation mode, a higher applied current consumed more energy to electrodialyze
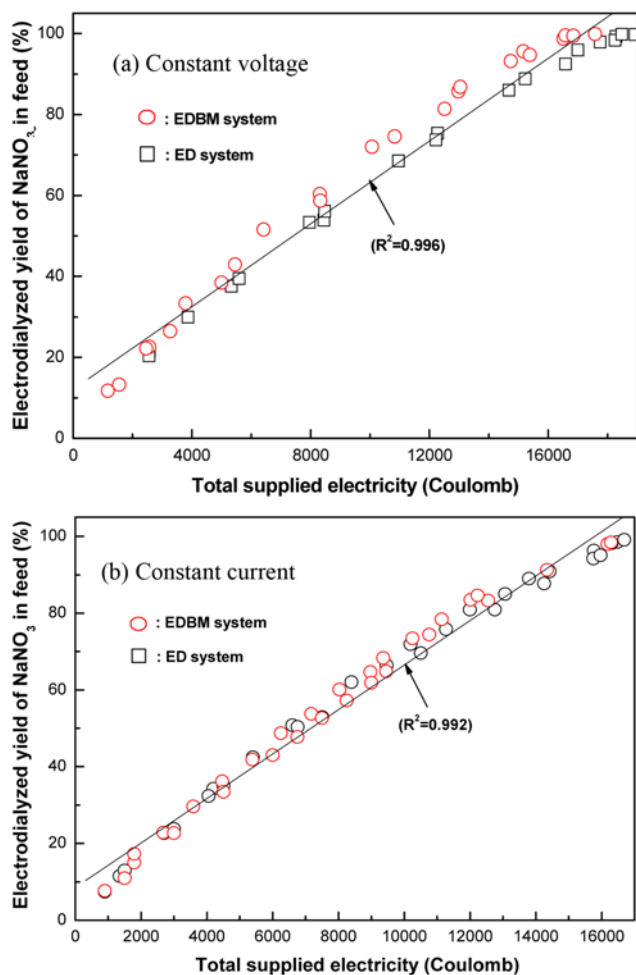
Fig. 6. Electrodialyzed yields of NaNO₃ in the feed solution with the total supplied electricity in the ED and EDBP systems under constant-voltage operation (a) and constant-current operation (b).

Fig. 7. Evaluated energy consumptions with the electrodialyzed yields of NaNO₃ in the feed solution in the ED and EDBP systems under constant-voltage operation (a) and constant-current operation (b).

the same amount of feed solution but also increased the electrodialysis rate. For the same applied current, the energy consumption of the EDBM system was much higher than that of the ED system for the same volume of feed solution despite the systems' identical electrodialysis rates, as shown in Figs. 4 and 5, because the total cell resistance of the EDBM system was higher than that of the ED system due to the bipolar membranes and electrode rinse compartments, as described above.

Fig. 8 shows the current efficiencies in the conventional ED and EDBM systems as a function of the electrodialyzed yield of NaNO₃ in the feed solution under constant-voltage (a) and constant-current (b) operation, which were evaluated using the results in Figs. 2 to 5. The current efficiency was calculated using Eq. (1) [9-11].

$$\text{Current efficiency} = \frac{Fz(\Delta C)V}{\int i(t)dt} \qquad (1)$$

where F, z, ΔC, V, i, and t are the Faraday constant (96,487 C/mole), ion valence, equivalent concentration change (N), solution volume (L), current (A), and time (s), respectively. In the ED and EDBM systems under constant-voltage and constant-current operations, the
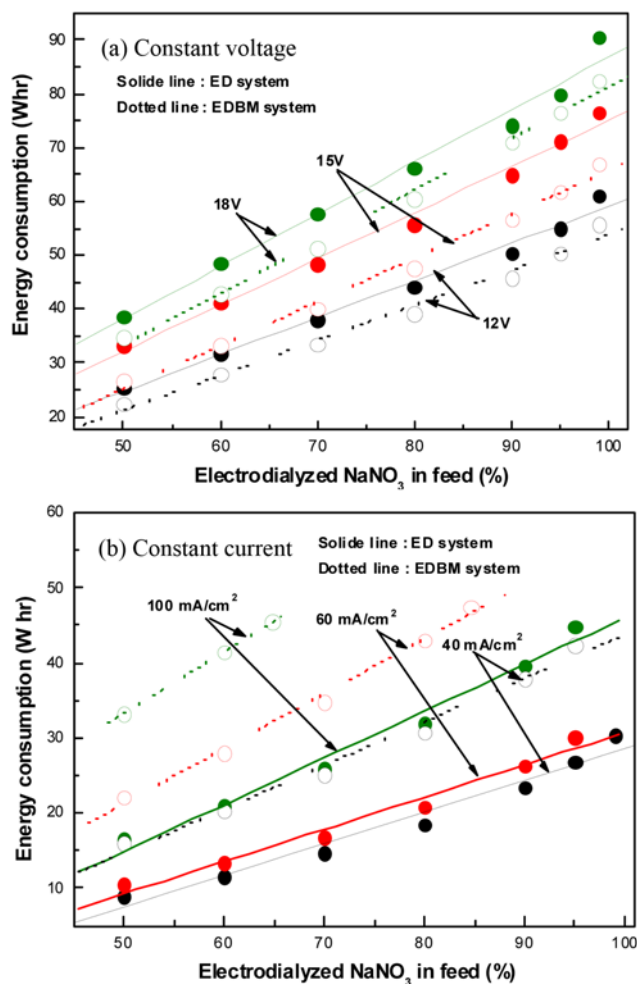
current efficiencies decreased with increases in the electrodialyzed yield of the feed solution. In constant-voltage operation, the current efficiencies were generally unaffected by the applied voltage. However, the current efficiency of the EDBM system was higher than that of the ED system for the same amount of feed solution. The reason for this difference is likely to be less back-attraction of OH⁻ ions in the basic compartment toward the feed compartment in the EDBM system, which requires less total electricity to recover the same concentration of NaOH by electrodialysis. In the constant-current operation, the current efficiencies were similar for the ED and EDBM systems and decreased with an increase in the applied current because the lower current flowing through the electrodialyzer causes fewer side reactions at the electrodes. Applying higher current in the electrodialysis system causes more heat generation due to the resistance components included in the system. In fact, the electrodialyzer was warmer for higher applied currents.

3. Evaluation of Resistances Characteristics of Individual Components Consisting of the Electrodialysis Systems

It is necessary to investigate how each component of the ED and EDBM systems affect the electrodialysis behaviors, such as the over-
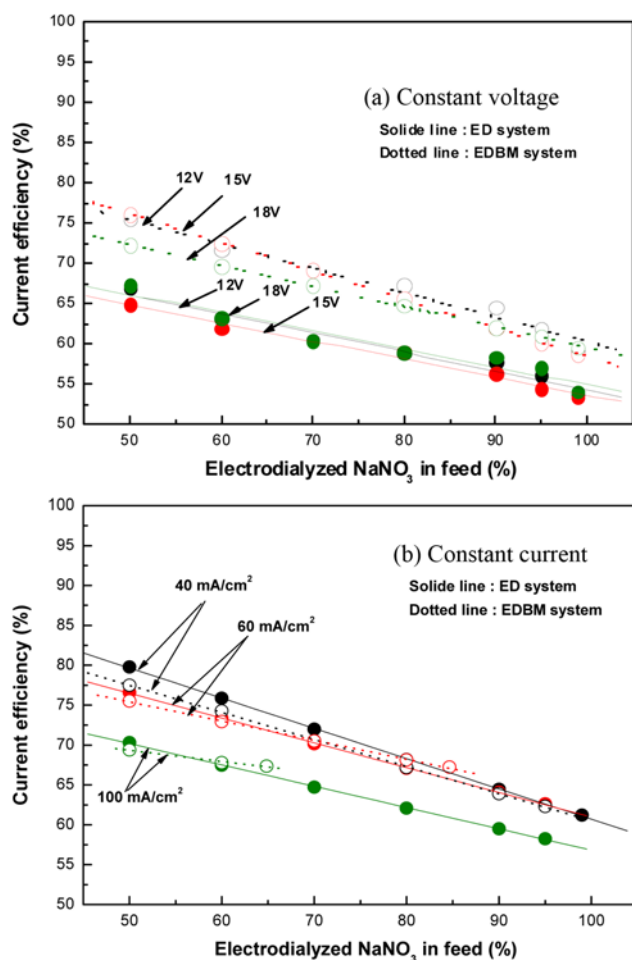
Fig. 8. **Current efficiencies with the electrodialyzed yields of NaNO₃ in the feed solution in the ED and EDBP systems under constant-voltage operation (a) and constant-current operation (b).**

all cell resistance, during the electrodialysis. The overall cell resistances of the ED and EDBM systems using an anode/cathode pair can be expressed as follows [9].

$$R_{cell\,for\,ED} = R_c + R_{c\,sol} + R_{CEM} + R_{f\,sol} + R_{AEM} + R_{a\,sol} + R_a \quad \text{for ED system} \quad (2)$$

$$R_{cell\,for\,EDBM} = R_c + R_{c\,rin\,sol} + R_{BPM} + R_{b\,sol} + R_{CEM} + R_{f\,sol} + R_{AEM}$$
$$+ R_{a\,sol} + R_{BPM} + R_{a\,rin\,sol} + R_a \quad \text{for EDBM system} \quad (3)$$

where R_c, and R_a are the resistances due to the cathode and anode; R_{CEM}, R_{AEM}, and $R_{f\,sol}$ are the resistances due to the cation exchange membrane, anion exchange membrane, and feed solution, respectively; $R_{c\,sol}$, and $R_{a\,sol}$ are the resistances due to the cathodic and anodic solutions in the ED system; $R_{b\,sol}$, and $R_{a\,sol}$ are the resistances due to the basic and acidic solutions in the EDBM system; and $R_{c\,rin\,sol}$, $R_{a\,rin\,sol}$, and R_{BPM} are the resistances due to the cathode and anode rinse solutions and the bipolar membrane in the EDBM system, respectively.

To calculate the individual resistances in Eqs. (2) and (3), the solution conductivities measured in the respective compartments in Figs. 2 to 5 were first evaluated to calculate the resistances of each solution in the electrodialysis system using Eq. (4).
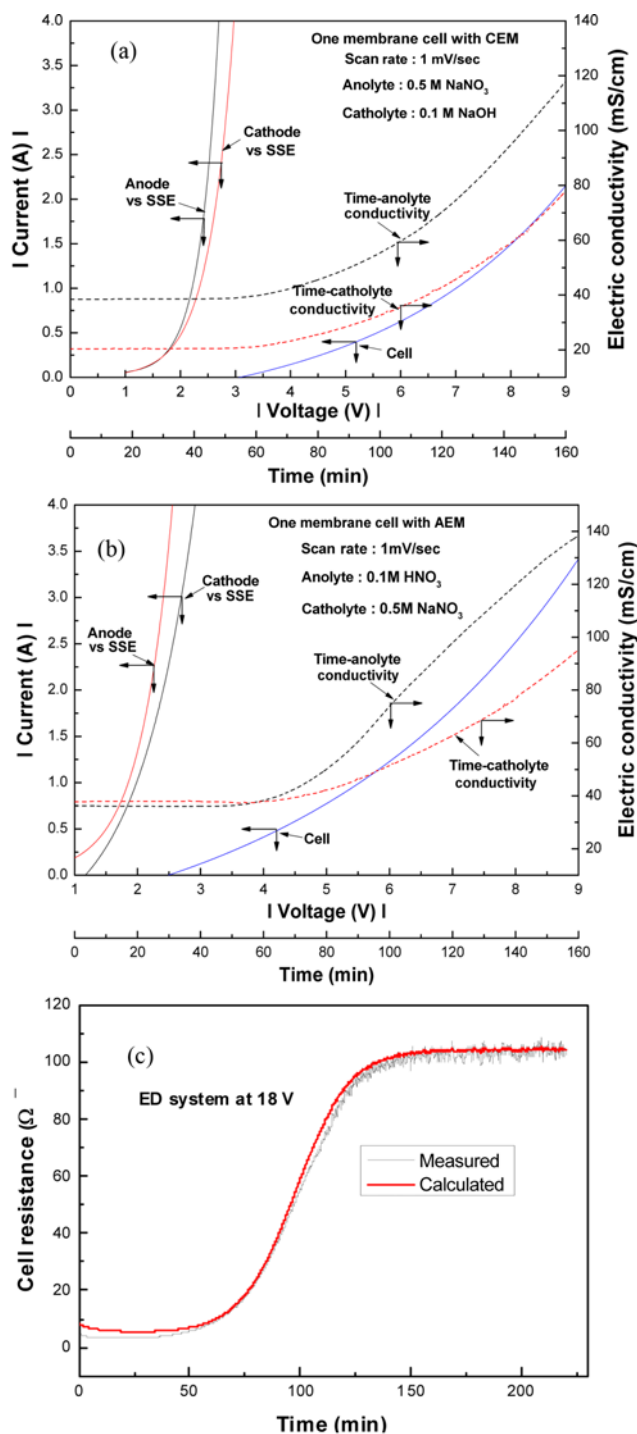

Fig. 9. **i-V curves at the anode and cathode vs. SSE, cell i-V curves, solution conductivities in the one-membrane cells with CEM (a) and AEM (b), and the measured and calculated overall cell resistances (c).**

$$R_i = \frac{1}{\kappa_i} \frac{l}{A} \quad (4)$$

where κ_i, l, and A are the specific conductance ($\Omega^{-1}\text{cm}^{-1}$), length (cm), and area (cm²), respectively. To evaluate the resistances of R_{CEM}, R_{AEM}, and R_{BPM} in Eqs. (2) and (3), several independent experiments were performed using a one-membrane cell in which the anode

and cathode were divided by a membrane (AEM, CEM or BPM) using the same membranes, electrodes, and solutions as in the electrodialysis experiments in Figs. 2 to 5. In the one-membrane-cell experiments, i-V curves were first measured at a scan rate of 1 mV/sec, and the conductivities in the anodic and cathodic chambers of the cell were measured at the same time as the curve measurements. The membrane resistance at a given current was calculated using Eq. (5).

$$R_{MEM} = R_{cell}\left(\frac{V_{cell}}{i_{cell}}\right) - R_{MEM\,a\,sol} - R_{MEM\,c\,sol}$$
$$- R_a - R_c\big|_{MEM=AEM,CEM,BPM} \qquad (5)$$

where R_{cell} is the overall cell resistance of the one-membrane cell and $R_{MEM\,a\,sol}$ and $R_{MEM\,c\,sol}$ are the resistances due to the anodic and cathodic solution of the one-membrane cell, respectively, calculated using Eq. (4). R_a and R_c are the resistances due to electrode reactions at the anode and cathode, respectively, during the electrodialysis for the one-membrane cell, which can be used for the R_a and R_c values in Eqs. (2) and (3) as well. The R_a and R_c in the one-membrane cell at a given current were evaluated from the i-V curves measured at the anode or cathode, respectively, as working electrodes with a reference electrode (SSE: silver/silver chloride in 0.3 M KCl) in the one-membrane cell with AEM, CEM or BPM.

Fig. 9 shows the necessary steps, mentioned above, for a conventional ED system operated at 18 V as an example for the evaluation of each resistance of the components comprising the electrodialysis system. Fig. 9(a) and (b) show the i-V curves measured at the anode and cathode with the SSE reference electrode in one-membrane cells equipped with CEM (a) and AEM (b) together with the cell i-V curves measured between the anode and cathode in the cells at the same time. The right-hand y axes in Fig. 9(a) and (b) represent the conductivities in the anodic and cathodic chambers of the one-membrane cells measured during the measurement of the i-V curves. From the results of Fig. 9(a) and (b), the membrane resistance by CEM or AEM at a given current could be evaluated using Eq. (5) and then used for R_{CEM}, and R_{AEM} in Eq. (2). The R_{fsol}, $R_{c\,sol}$, and $R_{a\,sol}$ in Eq. (2) were evaluated from the solution conductivities in Fig. 2(d) at a given time. To this end, the current and conductivity at a given time were related using Fig. 2(a) and (d). R_c and R_a in Eq. (2) were evaluated from the i-V curves at the cathode vs. SSE in Fig. 9(a) and the anode vs. SSE in Fig. 9(b), respectively. Fig. 9(c) shows the overall cell resistance calculated by the summation of the individual resistances obtained as described above and the actual overall cell resistance from the current curve in Fig. 2(a) measured during the electrodialysis at 18 V in the ED system. The measured and calculated overall cell resistance curves agree well with each other, which indicates that the method used to evaluate the individual resistances of the ED system during the electrodialysis was sound.

The same manipulations as that performed in the case of ED system at 18 V were carried out for the ED system operated at 40 mA/cm^2 and the EDBM system operated at 18 V and 40 mA/cm^2. Figs. 10 and 11 show the simulated behaviors of the individual resistance components with time in the ED and EDBM systems operated at 18 V (a) and 40 mA/cm^2 (b), where those of anode and cathode, AEM and CEM, and two bipolar membranes were expressed as summations of the components, which were denoted as the electrodes, ion exchange membranes, bipolar membranes, respectively,

for simplicity. In the beginning of the electrolysis, the overall cell resistance was affected by several individual resistances in the electrodialysis. The resistance fraction due to the electrode was generally higher than those due to the other components, such as the AEM and CEM, cathodic and anodic solutions in the ED system (or basic and acidic solutions in the EDBM system). In the EDBM system, the bipolar membranes were the most important in the overall cell resistance before the resistance due to the feed solution rapidly increased. However, after some electrodialysis time, in both the ED and EDBM systems, the times when the resistance fraction due to feed solution began to increase in Figs. 10 and 11 were very similar to those when the pH of the feed solution increased rapidly in Figs. 2 to 5. This point revels that the conductivity of the feed solution greatly affects the overall cell resistance, i.e., the behavior of cell voltage, after approximately 50% of the ions in the feed solution had migrated, as mentioned above.

CONCLUSIONS

An increase in the pH of the feed solution after an initial decrease, considered to be due to the hydroxyl ions generated in the cathodic compartment or basic compartment back-attracted toward anode
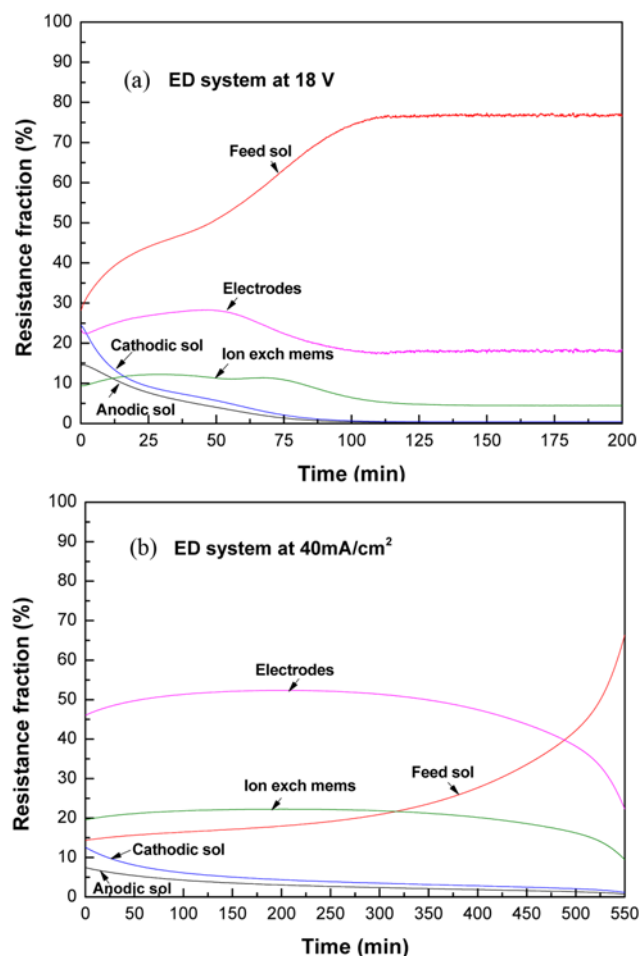

Fig. 10. Simulated behaviors of individual resistance components in the ED system operated at 18 V (a) and 40 mA/cm^2 (b) as a function of time.
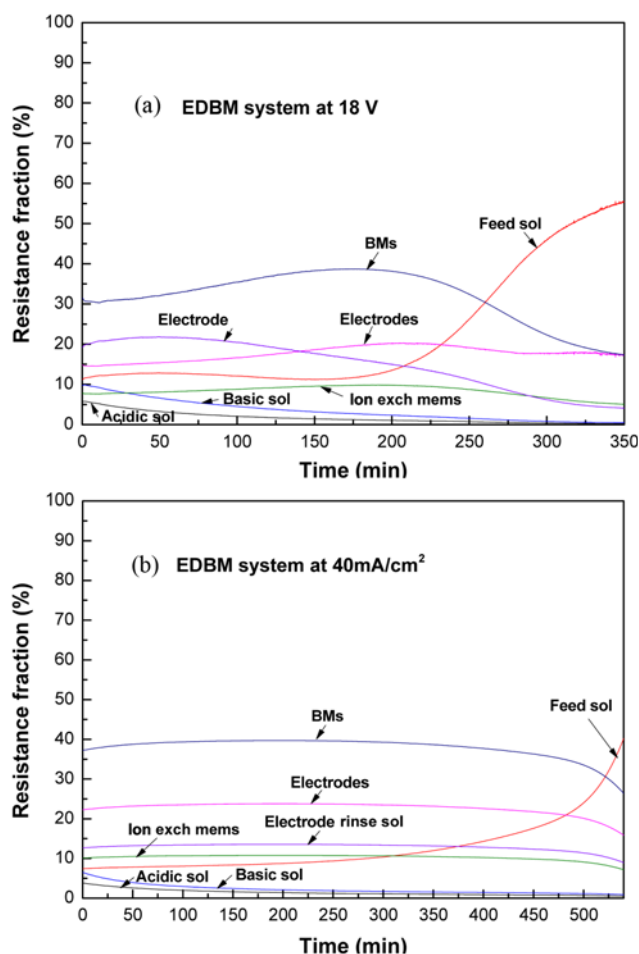
Fig. 11. Simulated behaviors of individual resistance components in the EDBM system operated at 18 V (a) and 40 mA/cm² (b) as a function of time.

through the cation exchange membrane, was observed in the ED and EDBM systems, which affected their energy consumption and current efficiency. The electrodialyzed extent for HNO_3 and NaOH recovery from $NaNO_3$ solution was almost proportional to the total amount of electricity supplied to the system, regardless of the operation mode, and electrodialysis system of ED and EDBM. The ED system was superior to the EDBM system with respect to energy consumption in constant-current mode, but the EDBM system was superior with respect to the current efficiency in constant-voltage mode. In the other cases, the ED and EDBM system showed similar performance. In both the ED and EDBM systems, the conductivity of the feed solution greatly affected the overall cell resistance after approximately 50% of the ions in the feed solution had migrated.

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