

Asymmetric Bipolar Membranes in Acid–Base Electrodialysis

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In this experimental study, the influence of asymmetric bipolar membranes on the salt impurities in the acid and base product is investigated. The thickness of one, the other, or both ion-permeable layers of a bipolar membrane is increased. With increased layer thickness, the current–voltage curves of the electro dialysis repeat unit recorded in a pilot-scale module show a reduced limiting current density, and thus they indicate an overall higher selectivity of these arrangements. Furthermore, these curves indicate water transport limitations for some membrane arrangements. Electrodialysis experiments with the same module at a high current density confirm the overall salt ion flux reduction. Moreover, these acid–base electro dialysis experiments directly reveal an increased asymmetry of the salt ion fluxes which can be utilized to design custom-made bipolar membranes with very high purity of either the produced acid or the base while keeping the bipolar membrane functioning without water transport limitations. The presented experiments also show that the bipolar membrane behavior can be characterized in situ, i.e., as a part of an electro dialysis repeat unit mounted in a pilot-scale electro dialysis module.

1. Introduction

Bipolar membranes are laminates of anion- and cation-exchange membranes and are used in a bipolar membrane electro dialysis module to split water for the production or concentration of acids and bases (Figure 1). Such acid–base electro dialysis has specific advantages compared to water splitting in membrane electrolysis. For example, the water splitting is not a reduction/oxidation reaction at electrodes but a forced dissociation of water by proton transfer inside the bipolar membrane. It becomes more viable as a technology in production processes when high product concentrations can be reached with reduced impurities. This paper deals with one major aspect, the purity of the products, which can be increased with improved bipolar membranes.

Like any ion-exchange membrane, the bipolar membrane or its respective ion-permeable layers contain co-ions, i.e., ions with the same electric charge as the functional groups of the ion-exchange material. These co-ions are responsible for the nonideal behavior of the membranes: for homopolar ion exchange membranes, i.e., separate anion- or cation-exchange membranes, this results in a reduced current efficiency and limited concentration factors. Salt ion leakage through bipolar membranes results in impurities of the acids and bases produced with bipolar membrane electro dialysis¹ (Figure 2). In general, the salt ion leakage into the acid is not the same as the salt ion leakage into the base;^{2–4} hence, the bipolar membranes show an asymmetric salt ion transport behavior. Information on the asymmetric salt ion fluxes in bipolar membrane electro dialysis is necessary to design suitable processes and improved bipolar membranes for specific application needs.

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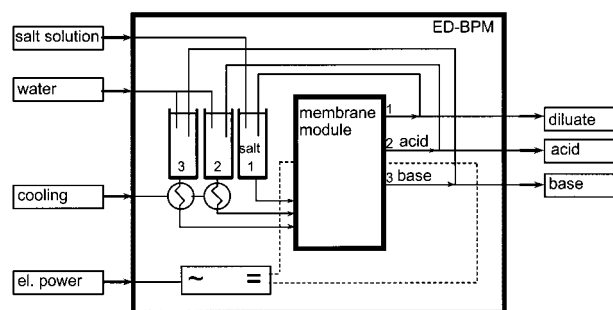


Figure 1. Flow scheme of bipolar membrane electro dialysis for the production of an acid and a base from a salt solution in a three-compartment electro dialysis module.

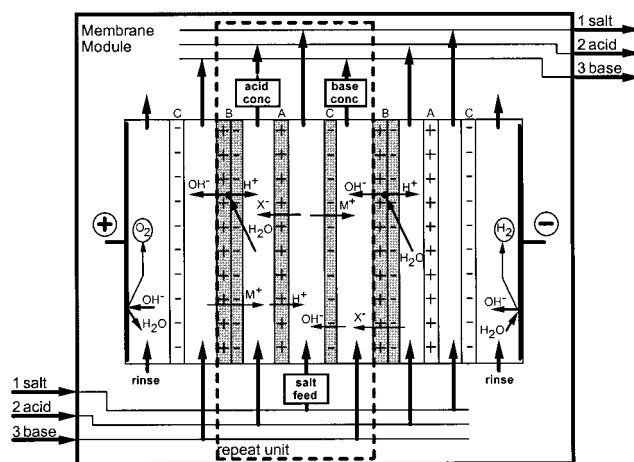


Figure 2. Scheme for a three-compartment arrangement of membranes and compartments in a module for bipolar membrane electro dialysis. In industrial membrane stacks, the repeat unit is repeated 20–50 times between one pair of electrodes.

In this paper, the control and directing of salt ion fluxes across bipolar membranes with increased asymmetry are demonstrated experimentally. Bipolar membranes are mounted together with cation- and anion-

exchange membranes in a pilot-scale electro dialysis stack to investigate the salt ion transport behavior in situ. The used heterogeneous bipolar membranes are not designed for high product purity but for economic use in ultrapure water systems;⁵ it is known that they show high salt ion fluxes, making them suitable to investigate flux improvements. The asymmetry of the membranes is altered by increasing the thickness of the bipolar membrane layers separately. Therefore, separate ion-exchange membranes of the same functionality are added, i.e., an anion-exchange membrane on the side of the anion-permeable layer or a cation-exchange membrane on the other side. Current–voltage curves are recorded to characterize the transport behavior of the repeat units, and short pilot-scale electro dialysis experiments are performed to quantify the salt ion transport. For both types of experiments, the same membrane arrangements in the membrane module are used, with the module mounted in the pilot-scale electro dialysis unit.

2. Theory

The salt ion fluxes in acid–base electro dialysis are closely related to the salt ion fluxes during measurements in salt solutions.¹ In both cases, the co-ion transport can be described with the same transport equations that relate the salt ion flux to the solution concentration and the membrane properties such as the apparent diffusion coefficient, the layer thickness, and the fixed charge density. When identical electrolyte or salt solutions are used, the current–voltage behavior of different membranes can be compared and guidelines for membrane development can be given. For a single membrane, the behavior in different electrolytes and with different concentrations can indicate transport limitations under certain operation conditions and the process design can be optimized. Below, first the salt ion transport in acid–base electro dialysis is described (section 2.1). Next, the characteristic values of current–voltage curves are correlated to the underlying transport processes (section 2.2).

2.1. Salt Ion Fluxes in Bipolar Membrane Electro dialysis. To obtain information on the membrane behavior in acid–base electro dialysis, the ion concentrations of the produced acid and base are recorded for progressing time. With that information, the current efficiency for the production of acid or base can be determined. If also the salt ion contents in the acid and base volumes are measured for different times, then the salt ion flux can be determined as well.

The following estimate of salt impurities in the base can be derived analogously to the salt impurity in the acid. The initial concentrations of hydroxide and salt in the base compartment and batch volume are known. The salt ion flux across the bipolar membrane is the property of interest and will be determined from an increase of the salt anion concentration in the base.

Therefore, the material flow balance over the base compartment shown in Figure 3 is used:

$$dc_{X,b} V_b/dt = A_{\text{eff}}(J_{X,\text{CEM}} - J_{X,\text{BPM}}) \quad (1)$$

Here, $c_{X,b}$ is the concentration of the salt anion X^- in the base compartment with the volume V_b ; the concentration is changing with time t . $J_{X,\text{CEM}}$ and $J_{X,\text{BPM}}$ are the fluxes of the salt anion across the cation-exchange membrane and the bipolar membrane, respectively. The

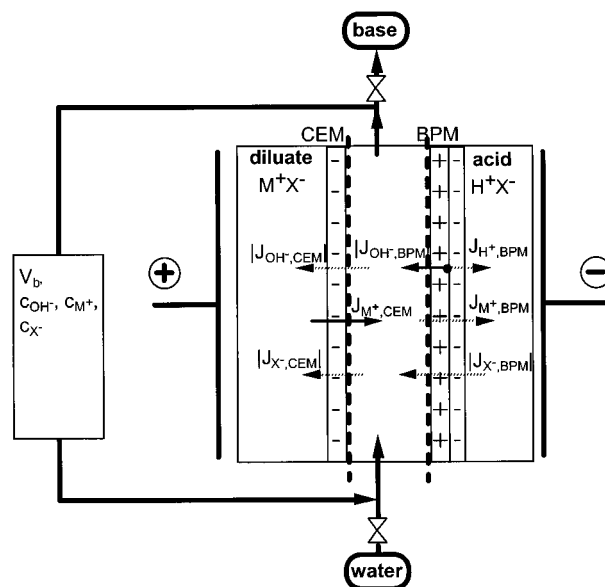


Figure 3. Scheme used for the material balance of the base compartment including the recycle reservoir during acid–base electro dialysis. The boundaries of the balance are indicated with the dashed lines and the (closed) valves. During the batch cycle time, the two valves at the inlet for the water and the outlet for the base product are closed. Full arrows denote desired ion fluxes; dotted arrows indicate ion leakage processes.

effective membrane area A_{eff} is the permeable area of one membrane multiplied by the number of repeat units. The material balance can be integrated in time if it is assumed that the fluxes are independent of time. This is the case if we can assume that a perfectly constant current is set and that the membrane transport properties are not affected by variations in solution concentrations. The latter assumption holds if in the design of the experiments high concentrations and large recycle volumes are used. The concentration of anions X^- in the acid is much higher than that in the base; thus, the flux of anions across the cation-exchange membrane in Figure 3 is much smaller than the flux across the bipolar membrane. When the anion flux across the separate cation-exchange membrane is neglected, the acid anion flux across the bipolar membrane can be estimated from the measured changes in volume and concentration.

$$-J_{X,B} = \frac{c_{X,b}(t) V_b(t) - c_{X,b,\text{initial}} V_{b,\text{initial}}}{A_{\text{eff}}(t - t_{\text{initial}})} \quad (2)$$

$J_{X,B}$ in eq 2 is the anion flux across the bipolar membrane depending on the actual conditions in the membrane compartments. These conditions—especially the initial concentrations in electro dialysis experiments—are difficult to control from one experiment to the other. Especially pilot-scale units have dead volumes that result in concentration variations. For the comparison of different membranes or membrane arrangements, either a concentration-independent “permeability coefficient” of the membrane should be found or the fluxes should be normalized to a standard concentration. To achieve this, the equation relating the salt ion fluxes to the solution concentration as developed in ref 1 for a quasi-symmetric bipolar membrane is utilized:

$$J_{M^+} = -J_{X^-} = \frac{D_{\text{mem}}(c)^2}{s c_{\text{FIX}}} \quad (3)$$

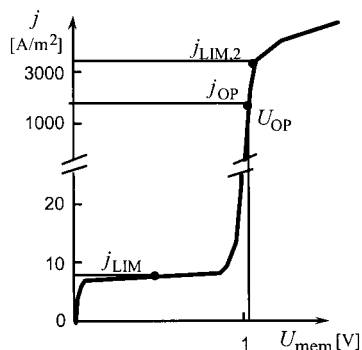


Figure 4. Schematic current–voltage curve of a bipolar membrane in a salt environment. Included are the limiting current density j_{LIM} , the operation current density j_{OP} , and the upper limiting current density $j_{\text{LIM},2}$.

Equation 3 represents the salt cation flux, J_{M^+} , and the salt anion flux, J_{X^-} , across a quasi-symmetric bipolar membrane in acid–base electro dialysis. The term $D_{\text{mem}}/sC_{\text{FIX}}$ can be interpreted as a constant membrane parameter; the apparent diffusion coefficient in the membrane D_{mem} and, moreover, the fixed charge density C_{FIX} and the layer thickness s do not depend significantly on the solution concentration. Thus, assuming the parameters are constant for small changes in solution concentration, we find that the fluxes are proportional to the square of the product solution concentration, i.e., the hydroxide ion or proton concentration. The flux of the salt anion into the base depends on the acid concentration, whereas the salt cation flux depends on the base concentration. For example, the salt cation flux into the acid is normalized to a freely chosen normal base concentration $c_{\text{S,b, norm}}$ according to

$$J_{\text{M}^+, \text{B, norm}} = J_{\text{M}^+, \text{B}} \left(\frac{c_{\text{S,b, norm}}}{c_{\text{S,b}}} \right)^2 \quad (4)$$

Here, the actual product concentration, the base concentration $c_{\text{S,b}}$, does not change considerably when large recycle volumes are used, the initial concentrations are high, and the total time of the experiment or between taking samples is rather short.

2.2. Current–Voltage Curves of Electro dialysis Repeat Units. The current–voltage curve of a single bipolar membrane recorded in a neutral salt solution (Figure 4) shows characteristic parts that correspond to known transport phenomena:^{1,6} below the (lower) limiting current density, only the salt ions transport the current; above this current density, also water splitting products are available to transport the current. At the limiting current density, the interface region of the two layers of the bipolar membrane is fully depleted of co-ions but water splitting has not yet started. Thus, the electrical resistance is the highest. In the current–voltage curve, this is the point with the smallest slope ($\Delta j/\Delta U$). The operating current density is chosen as high as possible to reduce the relative salt ion transport and to have a high water splitting efficiency. Above the upper limiting current density, the water transport toward the bipolar membrane junction is not sufficient to replenish the water split at the corresponding rate.⁷

The current–voltage curves can be recorded with a fully equipped electro dialysis module, without reference electrodes. Then all of the present elements such as electrodes, block solutions, membranes, concentration gradients, solutions, spacers, and the water splitting

reaction contribute to the electric potential difference across the working electrodes. The contribution of each element can be estimated for a given stack geometry and operating conditions.

Here, the main interest lies in the salt ion fluxes across the bipolar membrane. As derived in ref 1, the total salt ion flux is related to the limiting current density of the bipolar membrane. Also in an asymmetric membrane, the current below the limiting current density is transported by the salt ions. The current density is the same in the entire stack; thus, the limiting current density does not have to be corrected for the other elements in the module when stray currents can be neglected. Such stray currents are reduced as far as possible by using a long connection between the electrode rinse compartments and by having thin, long distributor channels in the frames of the membrane compartments in the module. To make the limiting current density clearly visible, the current–voltage curve of the electrodes and the end compartments of the electro dialysis module is recorded separately without any repeat unit.

Also other elements in an electro dialysis module can show a limiting current. Examples are the boundary layers in the salt feed chamber next to the cation- or anion-permeable membrane or at the electrodes (see Figure 2). The experimental conditions can easily be adjusted to make the limiting current densities of the two interfaces in the depleted compartment higher than the limiting current density of the interface in the bipolar membrane. This is achieved by using a high solution concentration and a sufficiently high flow rate through this compartment. When in the diluate compartment an electrolyte with the same salt concentration is circulated as in the acid and base compartments, the limiting current densities here in general are much higher than the limiting current density of a bipolar membrane. The reason for this is that in a bipolar membrane the entire ion-permeable membrane layer is the depletion layer, which has a thickness on the order of tens to hundreds of micrometers. Moreover, only a relatively small amount of co-ions present in this layer has to be removed to reach full depletion. In contrast, the hydrodynamic boundary layers next to electrodes and ion-permeable membranes are only a few micrometers thick, depending on the flow conditions in the cell. The true origin of a limiting current density can be identified by varying the flow rate through the compartments: the limiting current density of a bipolar membrane is independent of the flow rate because it is a result of the so-called internal concentration polarization within the membrane layer itself. On the other hand, the limiting current density of a solution boundary layer is independent of the membrane layer thickness.

3. Experimental Section

3.1. Electro dialysis Unit and Membranes. The current–voltage characterization and the electro dialysis experiments are both performed in the same electro dialysis unit and membrane arrangement in the membrane module as those used for the acid–base experiments. The electro dialysis unit is a customized, semiautomated pilot-scale system from FuMA-Tech (Vaihingen Enz, Germany) with five recycle loops. It is used in batch-recycle mode for the presented experiments.

The current and electrical potential across the stack are recorded and controlled by a computer. For the three

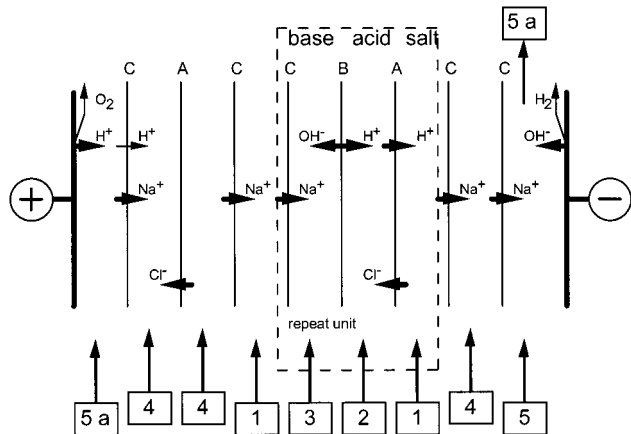


Figure 5. Membrane arrangement in the pilot module as used in these experiments. Either two or no repeat units are used: (A) anion-permeable membrane; (B) bipolar membrane; (C) cation-permeable membrane. Recycle streams: (1) salt diluate; (2) acid; (3) base; (4) block solution; (5) electrode rinse. The thick arrows indicate the desired ion transport across the ion-exchange membranes or membrane layers.

recycle streams in bipolar membrane electro dialysis (acid, base, and diluate), the temperature and the conductivity are displayed. The pH of these streams is not measured online, but when samples are taken in certain time intervals, the proton or hydroxide ion concentrations are determined by titration in the acid–base electro dialysis experiments. A laboratory cooler with a heat exchanger in the acid and base compartments is used to limit the temperature changes due to the resistance when operating at high current densities in the module.

The effective area for each membrane in the module (ED0/4 from FuMA-Tech) is $0.1 \text{ m} \times 0.18 \text{ m} = 180 \text{ cm}^2$. We use two repeat units with a three-compartment setup between the stainless steel cathode and the platinized titanium anode. A fourth stream, the so-called block solution, i.e., compartment 4 in Figure 5, is added to trap the reaction products from the electrodes to keep their influence on the actual separation small. Together with the electrode rinse solution, all five recycle streams of the electro dialysis unit are in use.

All of the ion-permeable membranes in these investigations are of the heterogeneous type from FuMA-Tech. The extra layers added to the bipolar membrane are heterogeneous anion- and cation-permeable membranes as well. Unfortunately, we cannot provide data on the thickness or composition. We know they are not optimized for bipolar membrane electro dialysis with respect to the salt ion leakage but can serve as good examples.

3.2. Recording Current–Voltage Curves. First, the current–voltage ($j-U$) behavior of the arrangement without any repeat unit is measured to obtain a current–voltage curve of the electrode compartments and the block solution. Next, the repeat units are introduced, and the $j-U$ curve is measured again. The difference between the two curves for the same current density is the current–voltage behavior of the repeat units in the module. The limiting current density of the membranes is indicated by the minimum slope (dj/dU) of the current–voltage curve.

In our experiments, 5 L of a 2 mol/L sodium chloride solution is used in each of the compartments 1–4; for the electrode rinse compartment 5, 0.5 M Na_2SO_4 is

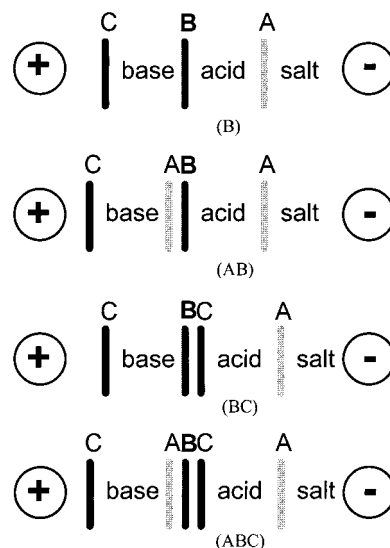


Figure 6. Repeat units as used for these experiments. The letters above the membranes separating the base, acid, and salt (or diluate) compartments indicate the types of ion-exchange membranes: (B) standard three-compartment arrangement (the cation-permeable side of the bipolar membrane faces the acid compartment); (AB) extra anion-exchange membrane attached to the anion-permeable side of the bipolar membrane; (BC) cation-exchange membrane attached to the cation-permeable side; (ABC) anion- and cation-exchange membrane to the respective sides of the bipolar membrane.

used. In the compartments 2 and 3 next to the bipolar membrane, $2 \times 1 \text{ L}$ of measurement solutions is recirculated for at least 10 min. This procedure ensures stable initial conditions for the salt solution experiments. The dead volume in each recirculated loop is approximately 0.2 L. It would be possible to connect the three compartments to one reservoir to keep the salt ion concentration constant during one experiment. However, then additional stray currents occur through the connecting tubes. These are avoided with the separate recycle loops. The relatively large recirculated volumes reduce the influences of concentration changes.

With the computer program, the voltage across the stack is set to a safety limit of 30 V and the current or current density is increased stepwise. The current–voltage curve is recorded with 40 steps of 6 min/step up to a current density of 8 mA/cm^2 and 3 min/step above.

To increase the asymmetry of the bipolar membrane, the repeat unit of membranes in the standard arrangement $\{C|\text{base}|B|\text{acid}|A|\text{salt}\}$ in Figure 5 is replaced by the repeat units in Figure 6 by adding extra membranes directly on the respective sides of the bipolar membrane. The arrangement “B” is the bipolar membrane with the necessary anion- and cation-permeable membranes separating the feed compartment from the acid and base compartments, respectively. The other arrangements are obtained by adding an anion-permeable membrane “A” at the anion-permeable side of the bipolar membrane and/or a cation-permeable membrane “C” at the cation-permeable side of the bipolar membrane, resulting in the arrangements “AB”, “BC”, or “ABC”. The extra layers are added to the bipolar membrane while all membranes are immersed in a sodium chloride solution to avoid air bubbles in the interfaces. Current–voltage curves are recorded for all four arrangements of the repeat units.

3.3. Procedures for Electro dialysis Experiments. The same bipolar membrane electro dialysis pilot module

is used for producing sodium hydroxide and hydrochloric acid with the membrane arrangements as shown in Figure 5. Therefore, the salt anion concentration in the base and the salt cation concentration in the acid are measured during an electro dialysis experiment with the same bipolar membranes, and also with increased asymmetry where possible. Of the arrangements in Figure 6, this was possible with the desired current density of 100 mA/cm^2 only for the arrangement B with the standard three-compartment repeat unit and for the arrangement AB with an extra anion-exchange membrane at the anion-permeable side of the bipolar membrane. The acid anion flux and the base cation flux are calculated as described in section 2.1 from the acid and base concentration time development in the product chambers.

The electro dialysis experiments are performed batch-wise at a current density of 100 mA/cm^2 , starting with approximately 2 mol/L solutions. A sodium chloride salt solution is used again in the feed compartment (compartment 1 in Figure 5), while the acid and base compartments are filled initially with hydrochloric acid and sodium hydroxide solutions, respectively. Because of limited temperature control, the temperature increased during an experiment from $25 \text{ }^\circ\text{C}$ to approximately $30 \text{ }^\circ\text{C}$.

Because most bipolar membranes cannot be operated with acid and base at its two sides without a current flowing, a minimum potential has to be applied to prevent the recombination of hydroxide ions and protons to water in the membrane contact region. Such a recombination can lead to the destruction of the bipolar membrane because of the pressure increase if the formed water cannot leave the membrane. Then the layers separate, a phenomenon which is often called ballooning. Only membranes with high water permeability can withstand such treatment. Therefore, as a preventive measure, a voltage of 5 V has been applied during the initial rinsing with acid and base next to the bipolar membrane.

Besides the electric potential, also the pH, temperature, conductivity, and volume increase of the three main streams are recorded in time intervals for indicative purposes. However, most important are the measurements of the salt concentration in the acid and base every $30\text{--}60 \text{ min}$. Analysis for the sodium concentration is done by atomic adsorption spectroscopy (AAS); the chloride concentration is measured by high-performance liquid chromatography (HPLC). The concentrations of the acid and base of these samples are determined by titration.

4. Results and Discussion

4.1. Current–Voltage Curves. The current–voltage curve of the module with and without two standard electro dialysis repeat units of arrangement B are presented in Figure 7a. Subtracting the voltage measured for the electrodes and block compartments only (the module without any repeat unit) from the voltage for the complete module results in the polarization characteristics of the two repeat units alone. From this potential of the repeat units in Figure 7b, the limiting current density is read at the point with the sharpest increase of electric potential for a current increment. Further, the water dissociation voltage for the two bipolar membranes in series is obtained by extrapolating the overlimiting current branch to a current density

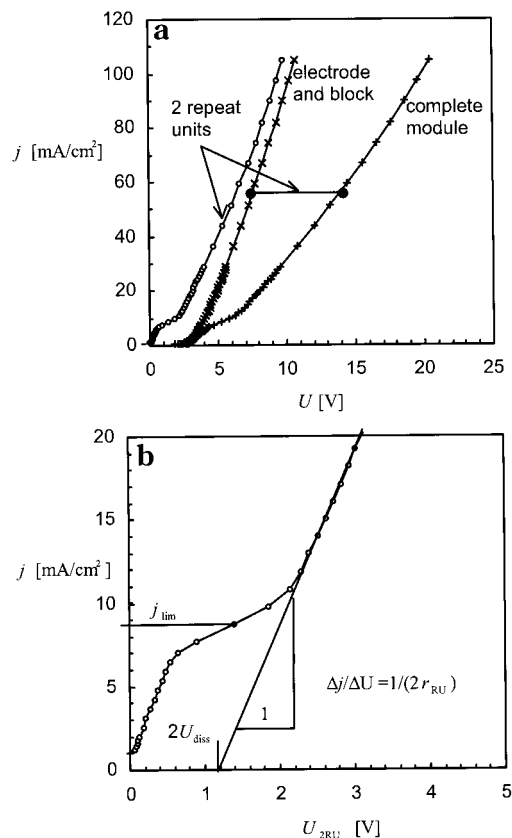


Figure 7. Current–voltage curve of the repeat units without block and electrode compartments for membrane arrangement (B): (a) subtracting the curves for electrode influences; (b) detail of the curves for two repeat units (reading the limiting current density j_{lim} , the water dissociation potential U_{diss} , and the area resistance of one repeat unit r_{RU}).

of zero. The area resistance of the two repeat units in series, $r_{2RU} = \Delta U_{2RU} / \Delta j$, is approximated by the inverse slope of the overlimiting branch (or its approximation by a straight line as used for determining the water dissociation potential).

Above the limiting current density, the water splitting products are increasing the overall number of ions in the system that are available to conduct the current. Furthermore, for current densities above about 40 mA/cm^2 , the temperature of the solutions is increasing slowly to about $35 \text{ }^\circ\text{C}$. This could not be prevented with the employed cooling system; the heat exchanger area was too small. Both effects result in a higher conductivity of the solutions and membranes. This can explain the slow increase of the slope of the overlimiting branches of the current–voltage curves in Figure 7a and arrangements B and AB in Figure 8a discussed below.

The current–voltage curves of the two repeat units with the four different bipolar membrane arrangements with increased thickness of the ion-permeable layers are presented in Figure 8 (corrected for the electrode and block solution contributions). Figure 8a shows the entire curves, while Figure 8b allows the focus on the low current density range to compare the limiting current density. The limiting current density of a bipolar membrane with an additional anion-exchange layer, arrangement AB, is almost reduced by a factor of 2 compared to the original bipolar membrane, but the ohmic resistance in the water splitting state is almost doubled (Figure 8a and Table 1). The current density of 100 mA/cm^2 could be reached with only a slightly

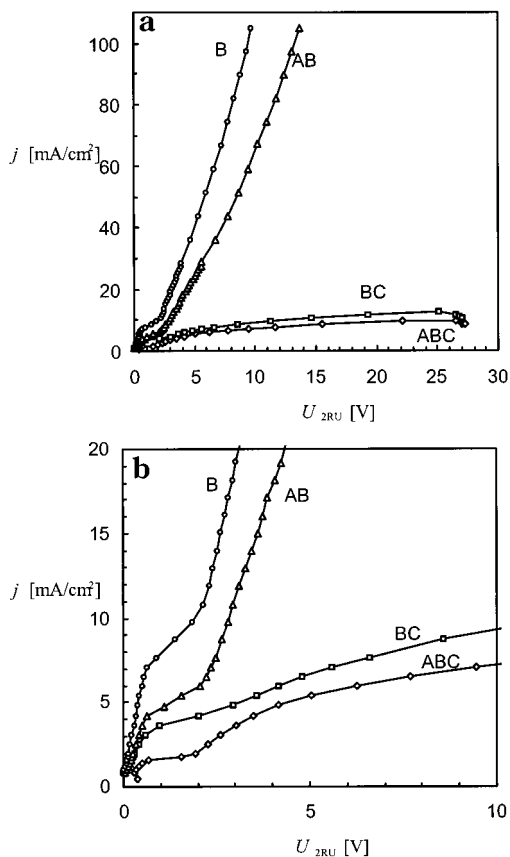


Figure 8. Current–voltage curves for the different bipolar membrane arrangements without and with extra ion-exchange membranes: (a) full curves; (b) detail around the limiting current density.

Table 1. Characteristics of Bipolar Membrane Arrangements (in 2.0 mol/L Sodium Chloride Solutions)

membrane arrangement	j_{LIM} [mA/cm ²]	U_{diss} [V] ^a	U_{RU} [V] at $j = 100$ mA/cm ²	r_{RU} [Ω cm ²]
B	9	0.64 ^a	4.7	46 ^a
AB	5	0.66 ^a	6.8	76 ^a
BC	4	<i>b</i>	<i>b</i>	<i>b</i>
ABC	1.8	0.39 ^c	<i>b</i>	300 ^c

^a Using the overlimiting branch up to $U_{2RU} = 7$ V. ^b No reading possible because of water transport limitation. ^c Using only the measurements between $U_{2RU} = 1.8$ and 3 V for extrapolation similar to Figure 7b.

increased voltage compared to the arrangement B because of the resistance of the extra layer. Thus, both arrangements can be operated at a current density of 100 mA/cm².

Also when an additional cation-exchange layer is applied in arrangement BC, the current–voltage curve shows a reduced limiting current density. The limiting current density is lower compared to the arrangement AB. If we assume the transport behavior of the thickened bipolar membrane layer becomes ideal, we can conclude the following: When the cation-exchange membrane (BC) is added, a stronger flux reduction of salt anions (or the co-ions in this layer) is observed compared to the flux reduction of cations observed upon adding the anion-permeable membrane (AB). This indicates that the original bipolar membrane in the arrangement B has a higher co-ion flux in the cation-permeable membrane layer compared to the co-ion flux in the anion-permeable layer. When both an anion- and a cation-exchange membrane are added on the respec-

tive sides, arrangement ABC, the limiting current density is further reduced as expected.

With the arrangement AB, it is possible to operate at current densities of up to 100 mA/cm². In contrast, the membrane arrangement BC shows a strongly increased voltage not far above the limiting current density (of 4 mA/cm²) at about 5 mA/cm²: the current density curve flattens off considerably; the electric potential is increasing significantly to values far above the water dissociation voltage. It is difficult to distinguish the two limiting current densities with this membrane arrangement. However, this second limitation appeared more clearly (also at about 5 mA/cm²) when additionally an extra anion-exchange membrane is added in the arrangement ABC. For this arrangement, the (first) limiting current density is much lower than the second limiting current density and two steps can be observed in Figure 8b. This upper limiting current density observed with the membrane arrangements BC and ABC is caused by the water transport limitation, leading to a dry-out of the membrane layers.⁷ Qualitatively, the dry-out was also observed by visual inspection when separating the extra membrane layer from the bipolar membrane after an experiment. The membranes at this contact seemed dry, whereas they were initially attached by loosely laminating them in a 2 mol/L sodium chloride solution (after equilibration in the same solution for more than 24 h). During normal operation with or without the extra anion-exchange membrane only (arrangements B and AB), the water flux through the cation-permeable membrane layer of the bipolar membrane is high enough to replenish the water used up in the water dissociation reaction in the bipolar junction. When the cation-exchange membrane is added on the cation-permeable side (arrangements BC and ABC) to increase its thickness, the water flux through this layer and from the opposite side through the anion-exchange layer is too small to sustain water splitting. These results indicate that the anion-exchange layer of the original bipolar membrane is almost impermeable to water. The reason for this is the low water content of this layer.

With a lower water content, the anion-permeable layer also contains fewer mobile co-ions than the cation-permeable layer. This supports the conclusion above that the flux of the co-ions in the anion-permeable layer is smaller than the flux of the co-ions in the cation-permeable layer of the original bipolar membrane. Furthermore, with a low water content, also the effective salt ion diffusion coefficients in the membrane phase are smaller. According to eq 3, this also reduces the flux of salt ions across the bipolar membrane.

One aspect that has not been addressed in the above discussion is the presence of additional unstirred layers between the loosely attached membranes. Because the effect of reduced limiting current density with increased layer thickness is also found in theory and for homogeneous membrane layers,¹ the observed transport phenomena are attributed to the change of the bulk layer properties. To what extent this holds for the water transport limitation could not be evaluated yet.

In summary, these experiments indicate reduced salt ion fluxes when attaching additional layers to the bipolar membrane. It can be concluded that the cation-permeable layer of the used original bipolar membrane contains much more water and more co-ions than the anion-permeable layer. This results in water transport

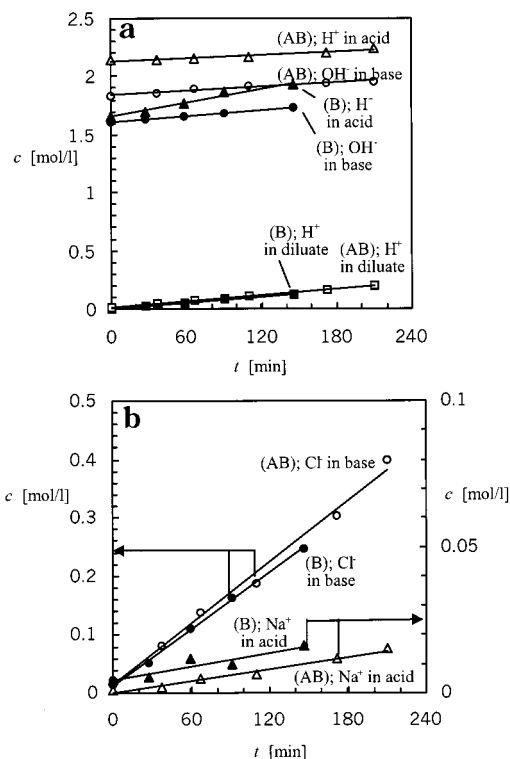


Figure 9. Concentration developments in the electrodiagnosis experiments with the arrangements B and AB: (a) product acid and base concentrations as well as the proton concentration in the diluate compartment; (b) concentrations of impurities in the products.

limitations when the cation-permeable layer becomes too thick. All of these membrane arrangements show a rather high limiting current density and, thus, a rather high salt ion flux compared to results obtained with a good bipolar membrane that have been reported earlier.⁶

The drastic reduction of the upper limiting current density in the case of an added cation-exchange membrane (arrangement BC) compared to the added anion-exchange membrane (AB) indicates that the differences between the transport properties of the two layers are very large. This means that the salt ion transport across this particular bipolar membrane is strongly asymmetric. Thus, in an acid–base electrodiagnosis experiment, it is expected to see a difference in the development of salt impurities in the base and in the acid.

4.2. Acid–Base Electrodiagnosis. The presented current–voltage characteristics in Figure 7 indicate that electrodiagnosis experiments at a current density of 100 mA/cm² are only possible for the original bipolar membrane B and the arrangement AB with the added anion-exchange membrane. The measured concentrations of the acid and base compartments are given in Figure 9. Because of the design of the experiment, starting with approximately 2 M base and acid, the concentrations of hydroxide ions and protons in the base and acid chambers, respectively, do not change much in time (Figure 9a).

The proton concentration in the salt or diluate chamber increases. This indicates the well-known phenomenon that the proton leakage across the anion-exchange membrane in general is higher than the hydroxide leakage across cation-exchange membranes.⁸ The reason is the increased mobility of the proton due to the tunneling effect.

Table 2. Measured Fluxes in Acid–Base Electrodiagnosis

membrane arrangement	J_{Cl^-} ^a [mol/(m ² h)]	J_{Na^+} ^a [mol/(m ² h)]	$ J_{Cl^-} /J_{Na^+}$	$J_{Na^+} + J_{Cl^-} $ [mol/(m ² h)]
B	15.8	0.8	20.0	16.6
AB	11.3	0.4	29.3	11.7

^a Normalized to 2 mol/L acid for anion flux and 2 mol/L base for cation flux by eq 4.

The chloride and sodium concentrations in the acid and base streams both increase significantly in time (Figure 9b). These ions form impurities in the products. The increase in salt ion concentration is used to calculate the fluxes in Table 2. We see in Figure 9a that the initial conditions of the experiments, the acid and base concentrations, are different. The large dead volumes of the system do not allow adjustment of the concentrations with higher accuracy. Therefore, we use eq 4 to normalize the flux of chloride ions to an initial acid concentration of 2 mol/L and the sodium flux to a base concentration of 2 mol/L. For the plain bipolar membrane B, the flux of salt anions into the base is about 20 times larger than the flux of salt cations into the acid (Table 2). Thus, its anion-permeable layer is much less permeable to co-ions than the cation-permeable layer. This is in agreement with the conclusions drawn from the current–voltage investigations.

When the anion-exchange membrane in the arrangement AB is added to increase the anion-exchange layer thickness, the transport of both salt ions and, thus, the total salt ion flux across the bipolar membrane is reduced. However, more interestingly, the ratio of the salt anion to the salt cation flux is increased significantly to almost 30 by adding this extra layer (Table 2). With an increased anion-permeable layer thickness, the flux of the co-ion in this layer (the base cation, Na⁺) is reduced more than the flux of the co-ion (Cl⁻) in the other layer.

Both the electrodiagnosis and the current–voltage measurements indicate flux reductions with increased membrane layer thickness. Both tests are required to evaluate a bipolar membrane in acid–base electrodiagnosis with increased layer thickness. The current–voltage curves can indicate transport limitations, but only the electrodiagnosis experiments can give an estimate of the actual salt ion fluxes and especially the flux ratio in an actual process.

The results remain qualitative because the fluxes depend not only on the actual concentrations and temperatures but also on the history or previous treatment the membranes have undergone before they are mounted in the stack. However, the results from this experimental study can be generalized to obtain rules on how a reduction of the salt impurities in one or both products can be achieved with other bipolar membrane arrangements, including other membranes and sequences. When an extra layer of ion-exchange material is added to the side of the bipolar membrane with the same functionality, the flux of the co-ion in this layer into the product on the other side of the bipolar membrane is reduced. The constraints found in this study are the reduced water permeability into the bipolar membrane interface, which has to remain sufficient, and the increased electrical resistance.

5. Conclusions and Recommendations

The presented experiments indicate that the bipolar membrane asymmetry can be increased and the sum of

salt ion fluxes decreased with an increased thickness of the layers of a bipolar membrane. With additional layers, the recorded current–voltage curves of the electro dialysis repeat unit show a reduced limiting current density, and thus they indicate an overall higher selectivity of these arrangements. Furthermore, these curves can also indicate water transport limitations, very important in investigating the technical feasibility of a bipolar membrane process. The electro dialysis experiments confirm the overall reduction of the salt ion fluxes predicted with the current–voltage curves. In addition, electro dialysis experiments reveal an increased asymmetry of the salt ion fluxes, information which cannot be obtained from current–voltage curves.

The used bipolar membrane has a very selective anion-permeable layer with a good anion/cation selectivity. The cation-permeable layer is highly water-permeable and mainly provides the water that is split in the interface. It already shows a strongly asymmetric salt ion transport with high acid anion fluxes compared to the base cation flux. This asymmetry is further increased by the added anion-permeable layer.

The presented methodology can be used to achieve salt ion flux reductions and to point out transport limitations for applications of bipolar membrane electro dialysis. The bipolar membranes can be tailor-made or modified such that the asymmetric salt fluxes allow production of very high purity acids or bases while keeping the bipolar membrane functioning without water transport limitations. The simplest method is adding readily available ion-permeable membranes to the respective sides of existing bipolar membranes. In such cases, both current–voltage characterization and electro dialysis experiments should be performed to investigate the technical feasibility. The experiments performed in this study indicate that the bipolar membrane behavior can be characterized in situ, for example, as part of an electro dialysis repeat unit mounted in a pilot-scale electro dialysis module.

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List of Symbols

c_{FIX} = fixed charge density of the cation- (anion-)permeable layer [mol/L]
 A = anion-exchange membrane or anion-permeable layer of a bipolar membrane
 A_{eff} = effectively permeable membrane area
 B = bipolar membrane

C = cation-exchange membrane or cation-permeable layer of a bipolar membrane

c_i = molar concentration of species i [mol/L]

D_{mem} = average apparent salt ion diffusion coefficient in the membrane layers [m^2/s]

j = current density [mA/cm^2]

J_i = flux of ion i (positive in the direction of positive current) [$\text{mol}/(\text{m}^2 \text{ s})$]

r = area resistance [$\Omega \text{ cm}^2$]

s = thickness [m]

t = time [s]

U = electric potential difference [V]

V = batch volume

Subscripts and Superscripts

a = acid compartment

b = base compartment

LIM = at the limiting current density of the bipolar membrane

mem = in or across the membrane

RU = repeat unit

S = solution

X = salt anion

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