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Behaviour of bipolar membranes at high current density Water diffusion limitation

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Abstract

In this paper the behaviour of bipolar membranes at very high current density is discussed. Current–voltage curves are determined, both for the Tokuyama Soda BP-1 and the WSI Technologies bipolar membrane. The current–voltage curves are characterised by an inflection point at which a drastic increase in resistance occurs. The inflection point is due to a limitation in the water supply into the bipolar membrane. The bipolar membranes are found to be damaged by applying current densities near and above the current density belonging to the inflection point. Measurements with the WSI membrane show that this damage primarily affects the anion exchange layer of the bipolar membrane. Furthermore, in this paper a qualitative comparison is made between calculated and experimental current–voltage curves. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Bipolar membrane; Current–voltage curve; Water transport limitation

1. Introduction

Frequently, bipolar membranes have been studied up to medium current densities (i.e. 100 mA/cm²). This region is important in rationalising the water dissociation mechanism [1]. When it comes to practical applications, electro dialysis with bipolar membranes at high current densities is attractive because of improvements in current efficiency. In general, the current efficiency increases with increasing applied current density [2–4]. A high current efficiency of a bipolar membrane improves the total effectiveness of the electro dialysis system in obtaining high quality

concentrated acids and bases. Therefore, an investigation of the behaviour of bipolar membranes at high current density is of great practical relevance.

When an electric field is applied across a bipolar membrane, water dissociation takes place at the transition region between the two charged layers that constitute the bipolar membrane. Water dissociates into protons and hydroxyl ions which are removed from the transition region by the electric field [5]. Water consumed in this way is replenished by diffusion from the outer solutions through the two monopolar layers into the bipolar membrane interphase. An increase in current density requires a faster generation of charge carriers, i.e. protons and hydroxyl ions. In other words, the rate of water dissociation must increase when the current density is increased. This is accompanied by an

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increase in water consumption at the transition region. When the rate of water dissociation is faster than the supply of water, a transport limitation occurs. In this way it can be reasoned that, at a certain value of the current density the water dissociation occurs so fast that the transport of water into the bipolar membrane transition region cannot keep up and limits the water dissociation process. A limitation of water supply would result in a drying out of the bipolar membrane, which is highly undesirable since it will cause a drastic increase in the resistance [1,4]. However, experimental studies on the limitation of water supply into a bipolar membrane are very scarce in the literature.

In a previous paper [1] a model was described calculating bipolar membrane current–voltage curves. In this model the water dissociation is assumed to be a result of proton transfer reactions involving the functional groups of the bipolar membrane. It is also assumed that the reactions are enhanced by the electric field according to the second Wien effect.

In this paper the behaviour of two bipolar membranes at very high current density is investigated. This is achieved by measuring current–voltage curves. Furthermore, the influence of such high current densities on the membrane material is studied. The measured current–voltage curves are compared qualitatively with curves calculated using the water dissociation model described in ref. [1].

2. Experimental

2.1. Current–voltage curves

Current–voltage curves were determined with a six-compartment cell. The membrane arrangement in the cell is shown in Fig. 1. A 0.5 M Na_2SO_4 solution was used for electrode rinsing, a 1.0 M NaCl solution was used in the second and fifth compartment, while a 0.5 M NaCl solution was used as the starting solution in the two central compartments adjacent to the bipolar membrane. The solutions were pumped through the cell with a flow rate of 475 ml/min. Current was established

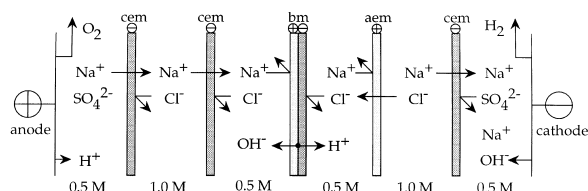


Fig. 1. Membrane arrangement and ideal ionic fluxes in the six-compartment cell (cem refers to a cation exchange membrane, aem to an anion exchange membrane and bm to a bipolar membrane).

through the membrane cell with a Delta SM 300-10D power supply (Delta Elektronika). The voltage drop across the membrane was determined by means of two Haber–Luggin capillaries connected to two colomel reference electrodes (Schott B2810). The area of the monopolar membranes was 23.76 cm². The bipolar membrane area was reduced by clamping the membrane between two glass plates with a circular hole of 4.74 cm² to allow the application of high current densities. The membrane cell and the experimental set-up are described in more detail elsewhere [6].

Two different bipolar membranes were used in the experiments. The first one is the BP-1 bipolar membrane supplied by Tokuyama Soda Inc. (Japan). This is a reinforced, single film membrane with a total thickness of 200 μm . The second membrane was supplied by WSI Technologies Inc. (USA) and is referred to as the WSI membrane. It consists of two separate non-reinforced membranes which have to be laminated together by hand to form the bipolar membrane. The thickness of the anion exchange layer is 43 μm , the thickness of the cation exchange layer 73 μm . The monopolar membranes used in the cell are the Tokuyama Soda AMX and CMX anion and cation exchange membrane, respectively.

2.2. Membrane characterisation

Characterisation of the monopolar layers of the WSI bipolar membrane involved the determination of the degree of swelling, the electrical resistance, the permselectivity and the ion exchange capacity. The degree of swelling was determined from the wet and dry weight of the polymer film according to: $\text{swelling} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$ [7].

The area resistance was determined under direct current by measuring the current–voltage relation in 0.5 M KCl both with and without the membrane (currents much smaller than the limiting current density were applied). The permselectivity was determined by the static method based on measurement of the membrane potential [7] when the membrane separates a 0.1 and 0.5 M KCl solution.

The ion exchange capacity was determined by titration. In case of the cation exchange layer a sample was brought into the proton form by immersion into a 1 M HCl solution for 24 h. The sample was soaked in ultrapure water to remove sorbed acid, after which the sample was placed in 2 M NaCl to exchange the protons with sodium ions. To ensure complete exchange, the NaCl solutions were renewed two more times. The NaCl solutions which now contained the released protons were combined and titrated with NaOH. The membrane was dried and the ion exchange capacity (meq/g) was calculated for the dry membrane.

For determination of the ion exchange capacity of the anion exchange layer, two different methods were used. The first method is similar to the procedure described above. The anion exchange membrane was first brought into the hydroxyl ion form by placing it in a 1 M NaOH solution for 24 h. After this the membrane was placed in a 2 M NaCl solution (which was renewed two times) to replace the hydroxyl ions by chloride ions in the membrane. The released hydroxyl ions were titrated with HCl. The second method was slightly different. In this case the membrane was brought into the hydroxyl ion form. After this the membrane was rinsed in ultrapure water and placed in a HCl solution. The hydroxyl ions now react with the protons of the HCl solution and the amount of unreacted protons remaining in the solution is determined by titration with NaOH. The ion exchange capacity was calculated from the difference between the initial proton concentration in the HCl solution and the final concentration (after reaction with the hydroxyl ions from the membrane).

rated with HCl. The second method was slightly different. In this case the membrane was brought into the hydroxyl ion form. After this the membrane was rinsed in ultrapure water and placed in a HCl solution. The hydroxyl ions now react with the protons of the HCl solution and the amount of unreacted protons remaining in the solution is determined by titration with NaOH. The ion exchange capacity was calculated from the difference between the initial proton concentration in the HCl solution and the final concentration (after reaction with the hydroxyl ions from the membrane).

3. Results and discussion

3.1. Measurements with the Neosepta BP-1 bipolar membrane

Fig. 2 shows two current–voltage curves measured with two different samples of the BP-1 bipolar membrane up to a current density of 600 mA/cm². This figure demonstrates that the voltage drop across the bipolar membrane remains fairly constant up to a current density of approximately 480 mA/cm². At this current density a clear inflection point is observed and a drastic increase in voltage drop is measured. The strong increase in voltage drop indicates a sharp rise in membrane resistance. The inflection point is due to a limitation of water supply into the bipolar membrane causing desiccation. The presence of an inflection point was also observed by Aritomi et al. [8] and Pivovarov and Greben [9]. Fig. 2 shows that the two measured current–voltage curves for the BP-1 bipolar membrane are very similar, indicating a good reproducibility.

The inflection point indicates a limited supply of water into the bipolar membrane. If, at a certain current density, the water concentration in the transition region has reached zero, no increase in current can be expected, i.e. a true limiting current density should be observed in the current–voltage curve. Fig. 2 shows that in practice this is not the case. Although the resistance increases drastically after the inflection point, still an increase in current density can be obtained. This demonstrates that

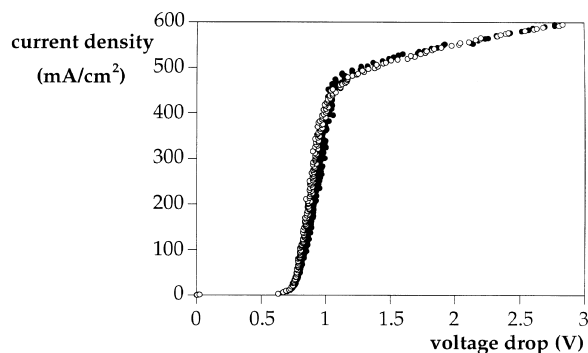


Fig. 2. Current–voltage curves measured up to high current density showing the presence of an inflection point at around 480 mA/cm². The two curves correspond to different samples of the BP-1 bipolar membrane.

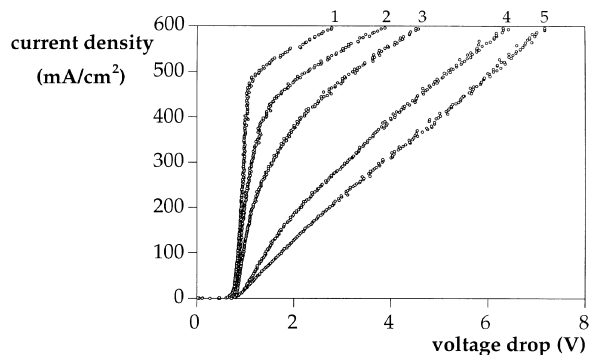


Fig. 3. Consecutive measurements of the current–voltage curve of a BP-1 bipolar membrane (numbers indicate the sequence).

at the inflection point the transition region is not completely depleted of water but the concentration is just so low that it limits the production of protons and hydroxyl ions.

When currents are applied that are larger than the current density belonging to the inflection point, the membrane performance is influenced. This was established by successive measurements of a current–voltage curve with the same membrane sample. Fig. 3 shows current–voltage curves measured five consecutive times up to a current density of 600 mA/cm². It is observed that a systematic change in the curves occurs. The curves are shifted to higher voltage drops and the inflection point not only moves to lower current densities but also becomes less distinct (and in fact cannot be observed in the last two measurements). The curves shifting to higher voltage drops indicates that the bipolar membrane resistance has increased. Apparently the bipolar membrane is damaged irreversibly when such high current densities are applied.

Fig. 4 shows that the inflection point occurring at high current density is not a well-defined point. The transition in slope in the curve is not instantaneous at a single current density but is a continuous trajectory over a certain current range. A deviation of the slope occurs between 350 and 400 mA/cm² (point marked B in Fig. 4), which is considerably smaller than the inflection point value of 480 mA/cm² determined by the intersection of the two slopes (point A).

Consecutive measurements were performed up

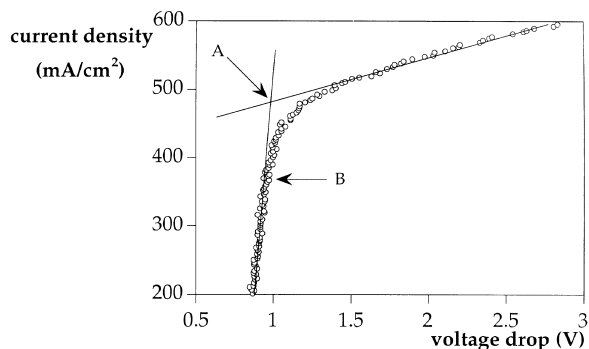


Fig. 4. Current–voltage curve showing the transitional region around the inflection point (A denotes the inflection point as determined by the two tangents, B refers to the onset of the transition).

to a current density of 400 mA/cm², which is smaller than the value of the current density belonging to the inflection point. The results are shown in Fig. 5. Here, similar features are observed as shown in Fig. 2, indicating that measurements up to 400 mA/cm² also damage the membrane. Consecutive measurements up to 200 mA/cm² did not show any change in current–voltage curve (not shown here). The measurements in Fig. 5 demonstrate that damage of the bipolar membrane starts as soon as a deviation occurs from the slope in the medium current range and that the transition in slope around the inflection point already indicates a permanent change in bipolar membrane resistance.

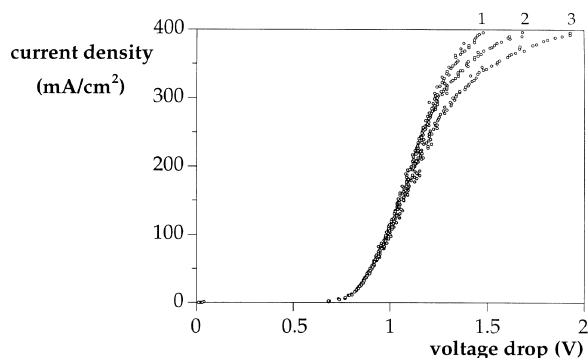


Fig. 5. Three consecutive measurements of a current–voltage curve for the BP-1 bipolar membrane up to 400 mA/cm².

3.2. Measurements with the WSI bipolar membrane

Fig. 6 shows two current–voltage curves measured up to 800 mA/cm^2 with two different samples of the WSI bipolar membrane. The current–voltage curves show a clear inflection point, similar to the findings with the BP-1 bipolar membrane. Fig. 6 also shows for both curves a rapid increase in voltage drop at lower current density, after which the voltage drop decreases again and a smooth curve is obtained. This irregular behaviour at lower current densities was not always observed. It is believed to stem from the structure of the WSI bipolar membrane. The membrane consists of two separate layers which have to be placed on top of each other prior to an experiment. This possibly results in a bad contact between the two layers with an irregular interphase and a thick water layer in between. When a current is applied, water is consumed at the interphase by the water dissociation reaction and the two layers are drawn to each other. In this way a better contact between the two layers is created, causing the resistance (voltage drop) to decrease again. Once a good contact is achieved, a smooth current–voltage curve can be obtained.

Comparing the two curves in Fig. 6 it is observed that the reproducibility for this membrane is much worse than in the case of the BP-1 bipolar membrane (Fig. 2). This might be due to an inhomogeneous distribution of the charged groups in the two layers created during membrane manufacturing or it might result from difficulties arising from

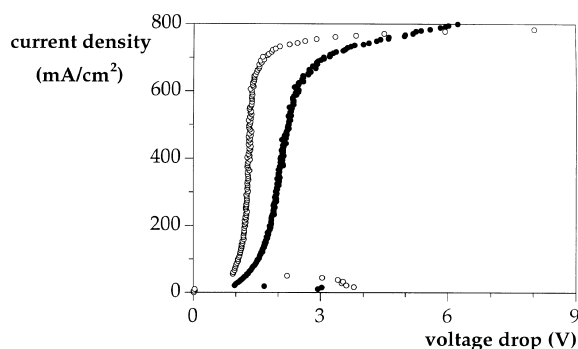


Fig. 6. Experimental current–voltage curves measured with two different samples of the WSI membrane.

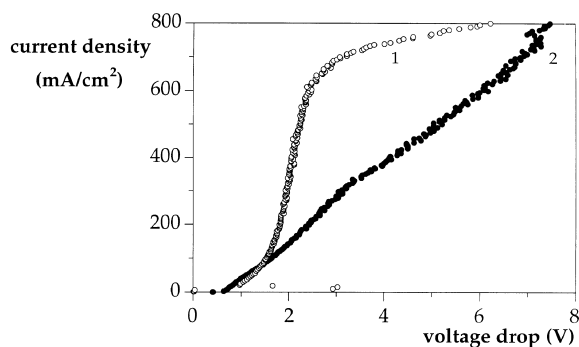


Fig. 7. Two consecutively measured current–voltage curves with the same sample of a WSI membrane.

the laminating procedure as described above. Although the two curves in Fig. 6 are different with respect to the voltage values, it is clear that the inflection points are located at similar current densities.

Also with the WSI membrane the influence of applying current densities above the inflection point was studied. Fig. 7 shows two consecutive measurements performed with the same piece of membrane. The results are similar to the results obtained with the BP-1 bipolar membrane. With the WSI membrane already the second measurement no longer showed an inflection point. Again the curve was shifted to higher voltage drops, indicating that the membrane was damaged in the first measurement after applying currents larger than the current density belonging to the inflection point. Comparing Fig. 7 and Fig. 3 it is clear that the change in current–voltage curve is much more pronounced in case of the WSI membrane.

3.3. The inflection point at high current densities

The presence of an inflection point in the current–voltage curves indicates that at a certain current density the resistance increases drastically, i.e. the amount of conducting ions (protons and hydroxyl ions) produced at the transition region becomes a limiting factor. In principle this limitation can be due to the two processes which are involved in the water dissociation.

(1) The increase in resistance might be due to a

limitation of the water dissociation reaction itself.

- (2) The inflection point might be related to the water transport into the bipolar membrane. If the water dissociation reaction is so fast that all the water at the interphase is consumed by the reaction before water is replenished from the outer solutions, a limitation of conducting ions would possibly occur as well.

Since the WSI bipolar membrane consists of two separate layers, experiments can be performed in which the thickness of the bipolar membrane can be varied by placing several monopolar layers on top of each other. The results are shown in Fig. 8. An increase in the thickness of the monopolar layers constituting the bipolar membrane results in a significant shift of the inflection point to lower current densities. This is a strong indication that the water transport into the bipolar membrane is the reason for the inflection point. Increasing the thickness of the bipolar membrane results in a longer diffusion pathway for water molecules and thus a limitation of the water supply (the inflection point) will occur at lower current densities.

This can also explain the difference in position of the inflection point when the WSI (inflection point around 720 mA/cm²) and the BP-1 bipolar membrane (inflection point around 480 mA/cm²) are compared. The BP-1 membrane is much thicker (200 μm) than the WSI membrane (total thickness

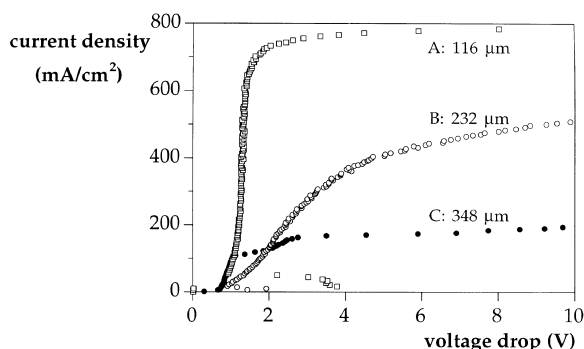


Fig. 8. Current–voltage curves of WSI bipolar membranes with varying thickness (membrane A: one cation plus one anion exchange layer; membrane B: two cation plus two anion exchange layers; membrane C: three cation plus three anion exchange layers).

116 μm). If similar water diffusion coefficients are assumed in both bipolar membranes, water diffusion limitation is expected to occur at a lower current density for the thicker, i.e. the BP-1, bipolar membrane.

The experiments described are in agreement with the work presented by Aritomi et al. [8]. They also concluded that the inflection point is related to a limited diffusional transport of water into the bipolar membrane interphase. This was based on experiments in which the bulk solution concentration was varied. The inflection point shifted to lower current densities with increasing solution concentration. The increase in salt concentration gives an increase in the osmotic pressure of the solution, resulting in a decreasing water supply into the membrane.

3.4. Physical or chemical cause of the damage

In the previous sections it was shown that both the BP-1 and the WSI bipolar membrane are irreversibly damaged (increase in resistance) when current densities near and above the inflection point are applied, the nature of this alteration being unclear. The highest resistance in a bipolar membrane is located at the transition region [10]. This is not only the region of low conductivity (deionised water layer) but also the region where drying out of the membrane is most likely to start when a limitation of water supply occurs. As a result an intense heat generation occurs at the transition region. This heat generation is easily detected by the increase in solution temperature next to the bipolar membrane (typically a temperature increase of 2 to 10°C was measured during the determination of a current–voltage curve up to very high current densities). In one of the experiments with the WSI membrane, heat formation was so intense that it completely burned away the membrane.

It is known that anion exchange membranes often display a limited chemical stability when placed in contact with alkaline solutions [11]. Kneifel and Hattenbach [12] performed long term stability experiments with different commercial ion exchange membranes. Exposure to an alkaline solution changed the resistance and the ion

exchange capacity of most of the membranes. Similar observations were obtained when placing the membranes in a NaCl solution at 85°C, showing that elevated temperatures can also affect the properties of the membranes. The changes were believed to be related to variations in or destruction of the polymer matrix or the destruction of ion exchange groups due to chemical reactions. It was found that acidic solutions hardly influenced the investigated membranes.

When a current–voltage curve is measured, a rapid change in pH of the solutions next to the bipolar membrane is observed. The pH of the solution in the base compartment (anodic side of the bipolar membrane) is typically in the range of 12 to 13 during an experiment when higher current densities are reached. Although the measurements are started with the two layers in the salt form, the intense generation of protons and hydroxyl ions will cause the anion exchange layer to be changed into the hydroxyl ion form. Therefore it can be assumed that a high hydroxyl ion concentration will be present in the anion exchange layer.

Experiments were performed in which the effect of creating a dry bipolar membrane and the effect of a treatment with NaOH were investigated. A BP-1 bipolar membrane was placed in a vacuum oven at 50°C for 14 days to remove all water from the membrane. Another BP-1 bipolar membrane was placed in a 0.5 M NaOH solution at room temperature for 20 h. Current–voltage curves were determined with the treated membranes and compared with an untreated bipolar membrane. The results are shown in Fig. 9. In this figure the curves of damaged membranes that were determined when performing consecutive measurements (same curves as in Fig. 3) are also shown.

Fig. 9 shows that not only is the resistance (voltage drop) of the pretreated bipolar membranes higher than for the untreated membrane (curve 1), but it is also clear that the inflection point is situated at much lower current densities. Thus the two curves of the pretreated membranes resemble the current–voltage curves of the membranes damaged by consecutive measurements (curves 2 and 3). Therefore, Fig. 9 demonstrates that both drying of the bipolar membrane and an exposure to 0.5 M

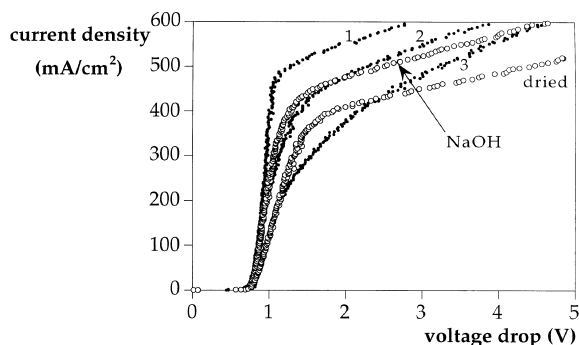


Fig. 9. Effect of pretreatment on the current–voltage curve of a BP-1 bipolar membrane. Curves 1 to 3 (closed circles) refer to three consecutively determined current–voltage curves (no pretreatment), the curve indicated with ‘NaOH’ refers to the bipolar membrane pretreated with a NaOH solution, ‘dried’ refers to the curve measured with the bipolar membrane that was dried prior to the experiment.

NaOH damages the membrane. However, no conclusions can be drawn as to which of the two (or a combination) are responsible for the damage occurring with a bipolar membrane when current densities near or above the inflection point are applied.

3.5. Localisation of the damage in the bipolar membrane

Drying out of the bipolar membrane is most likely to start at the transition region where the water dissociation reaction occurs. It is unknown whether damage of the bipolar membrane occurs only at the transition region (which is a very thin layer compared to the thickness of the monopolar layers) or if it extends to the bulk of the monopolar layers as well when currents near or above the inflection point are applied. An experiment was developed to establish whether the damage is only located at the transition region. The WSI membrane was damaged by measuring a current–voltage curve up to 800 mA/cm². After this, the membrane was turned inside out, i.e. the two sides of the bipolar membrane which originally faced the solutions now formed the transition region. If damage had occurred only at the transition region then it was expected that the bipolar membrane turned inside out would show a similar current–

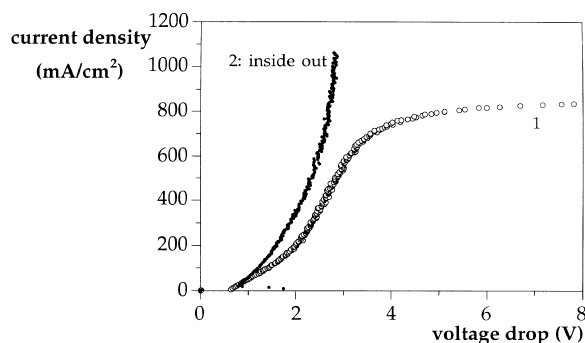


Fig. 10. Current–voltage curves of a WSI membrane. The membrane sample is first damaged by measuring curve 1. The current–voltage curve is then determined with the bipolar membrane turned inside out (2) and does not show an inflection point any more.

voltage curve as the first measurement. However, these experiments failed as it was found that the second measurement did not show an inflection point any longer in the current range investigated. An example of this behaviour is shown in Fig. 10. It is believed that the absence of an inflection point might be due to the presence of holes or cracks in the membrane which enable a large water transport into the bipolar membrane, thereby not showing any water diffusion limitation. The holes or cracks might be formed during the first measurement. It was also observed in one experiment that no inflection point was obtained even in the first measurement. The two layers of the WSI membrane are very thin and not reinforced, which results in a poor mechanical stability of this membrane.

Both for a new and a damaged WSI bipolar membrane the surface of the monopolar films

constituting the transition region was studied with attenuated total reflectance infrared (ATR-IR) spectroscopy. Assignment of the peaks to the charged groups in the films was found to fail due to interference with water present. Therefore, no information could be obtained about the nature of the damage in the bipolar membrane using this technique.

3.6. Characterisation of the monopolar layers of the WSI membrane

The advantage of using the WSI bipolar membrane is that it consists of two layers whose bulk properties can be determined separately. In this part the electrical resistance, swelling, permselectivity and ion exchange capacity of the two monopolar layers are compared for membranes as-received and membranes which are damaged. The damaged samples were obtained from the membranes that were used in measuring current–voltage curves up to current densities above the inflection point (typically up to 800 mA/cm²). An overview of the results is shown in Table 1 for the cation exchange layer and in Table 2 for the anion exchange layer. Each value in these tables was obtained with a different membrane sample.

Table 1 shows that the determined properties of the cation exchange layer of the WSI membrane are very similar for the new and the damaged membrane. Hence it seems that the bulk properties of the cation exchange layer are not affected when damaging the bipolar membrane.

In Table 2 the change in properties is shown for the anion exchange layer. Although a considerable spread in swelling values is observed, it seems

Table 1

Comparison between properties of the cation exchange layer of the WSI membrane as-received and the membrane that was damaged by applying current densities above the inflection point. Each value refers to a different membrane sample

Membrane status	Swelling (%)	Exchange capacity (meq/g dry)	Area resistance (Ω cm ²)	Permselectivity (%)
New	20.1	0.76	1.25	94.4
	25.0	0.87	1.36	95.0
	27.0			95.0
Damaged	22.7	0.72	1.01	93.3
	26.1	0.83	1.29	93.9
	27.8			95.0

Table 2

Comparison between properties of the anion exchange layer of the WSI membrane as-received and the membrane that was damaged by applying current densities above the inflection point [(1) determined according to method 1; (2) according to method 2 as described in the experimental section]. Each value refers to a different membrane sample

Membrane status	Swelling (%)	Exchange capacity (meq/g dry)	Area resistance ($\Omega \text{ cm}^2$)	Permselectivity (%)
New	30.2	0.87 (1)	0.23	81.5
	33.4	0.86 (1)	0.23	82.6
	34.7	0.51 (2)		95.0
Damaged	24.2	1.50 (1)	0.36	82.6
	26.2	1.46 (1)	0.39	81.8
	26.4	0.45 (2)		95.0

that the swelling of the damaged anion exchange layer is lower than for the new membrane. Simultaneously, it is observed that the area resistance seems to have increased for the damaged membrane. Swelling and area resistance are both properties which are closely related to the amount of fixed charged groups in an ion exchange membrane. A lower value of the swelling and a higher electrical resistance is an indication that the amount of fixed charges has decreased in the membrane. The determination of the ion exchange capacity of the anion exchange layer appeared to be difficult, as is shown in Table 2. Two methods were used to determine the ion exchange capacity of the anion exchange layer. According to the first method the ion exchange capacity of the damaged membrane was much higher than that of the new membrane, which is very peculiar. Not only can no explanation be given as to why the ion exchange capacity can increase when the membrane is damaged, but it also contradicts the finding that the bipolar membrane resistance increases when it is damaged. Therefore, the second method was used. With this method much lower values for the ion exchange capacities were obtained. Although the difference is small, the value for the damaged anion exchange layer was now found to be lower than for the new membrane, in agreement with a lower swelling and higher area resistance.

3.7. Model calculations

In ref. [1] a model was described calculating bipolar membrane current–voltage curves. The model assumes the water dissociation to originate

from proton transfer reactions involving weakly basic groups (tertiary amines) in the depletion anion exchange layer, enhanced by the electric field. Water reacted at the transition region is assumed to be replenished by a diffusional transport from the outer solutions into this region. In this section a qualitative comparison will be made between calculated current–voltage curves and the experimental curves determined up to current densities above the inflection point.

The main parameters in the model calculations and their assumed values are: the fixed charge density of the two layers (1.5 mol/l), the initial concentration of basic groups in the anion exchange layer (1.5 mol/l), the initial water concentration in the membrane (10 mol/l) and the thickness of the monopolar layers (100 μm for BP-1, 58 μm for WSI). The values of the rate constants in the proton transfer reactions are determined by the $\text{p}K_b$ of the basic groups [1]. For a detailed description of the various parameters involved in the calculations the reader is referred to ref. [1].

Fig. 11 shows calculated current–voltage curves, demonstrating the effect of the water diffusion coefficient. The shape of the curves resembles the experimental results to a large extent; also, the calculated curves show an inflection point at high current densities. The figure shows that a decrease in the water diffusion coefficient results in a shift of the inflection point to lower current densities. Fig. 12 shows the steady state water concentration at the transition region calculated as a function of the external voltage, corresponding to the calculated current–voltage curve with a water diffusion

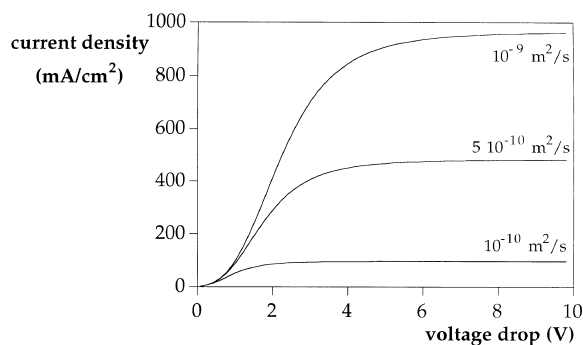


Fig. 11. Calculated current–voltage curves in which the value of the water diffusion coefficient is varied. For the calculations a pK_b of 5.0 was used as well as the parameters referred to in the text.

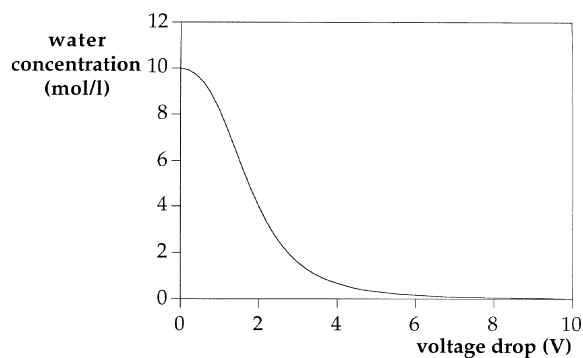


Fig. 12. Calculated steady state water concentration at the bipolar membrane transition region as a function of external voltage. The graph corresponds to the current–voltage curve calculated with a water diffusion coefficient of $5 \times 10^{-10} \text{ m}^2/\text{s}$ in Fig. 10.

coefficient of $5 \times 10^{-10} \text{ m}^2/\text{s}$ in Fig. 11. Comparing Figs. 11 and 12 shows that the inflection in the current–voltage curve is a result of the decreasing water concentration in the transition region. With increasing external voltage this water concentration gradually reaches zero. Simultaneously, the water dissociation becomes limited by the water supply and an inflection in the current–voltage curve occurs. In the calculations the water concentration truly reaches zero and therefore a true limiting current density is observed at high current density in the calculated current–voltage curves.

Fig. 13 shows the influence of the thickness of the monopolar layers on the calculated current–voltage curves. Increasing the thickness of the membrane results in a shift of the inflection point

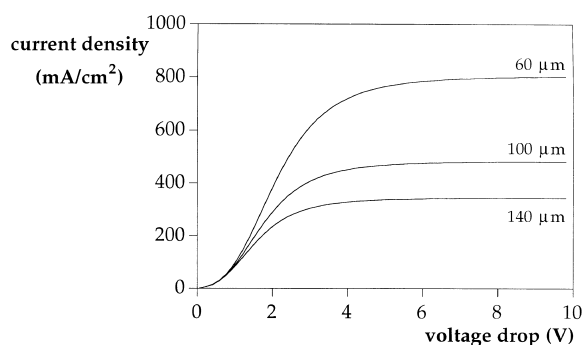


Fig. 13. Calculated current–voltage curves in which the thickness of the monopolar layers of a bipolar membrane is varied. For the calculations a pK_b of 5.0 and a water diffusion coefficient of $5 \times 10^{-10} \text{ m}^2/\text{s}$ was used.

to lower current densities. This is in agreement with the experimental curves shown in Fig. 8, where the thickness of the WSI membrane was varied.

Figs. 11 and 13 show, according to expectations, a decrease in the limiting current density due to both a decrease in water diffusion coefficient and an increase in membrane thickness, resulting in a smaller diffusional transport of water into the bipolar membrane transition region.

The experiments with the WSI bipolar membrane indicate that the damage occurring with the membrane at high current density mainly affects the anion exchange layer. The swelling decreases and the area resistance appears to increase. This might be due to a decrease in the amount of fixed charged groups present within the anion exchange layer. In ref. [1] it was described that the proton transfer reactions primarily occur at the anion exchange membrane. A reduction in fixed charge in the anion exchange layer of the WSI membrane would also result in a lower concentration of the basic groups involved in the water dissociation process. Fig. 14 shows the calculated effect of a decreasing concentration of these groups in the transition region. The current–voltage curve is shifted to higher voltage drops. This is the same trend as was observed experimentally when the bipolar membrane was damaged (see Figs. 3 and 7).

The damaged bipolar membranes not only showed an increase in resistance but it was also

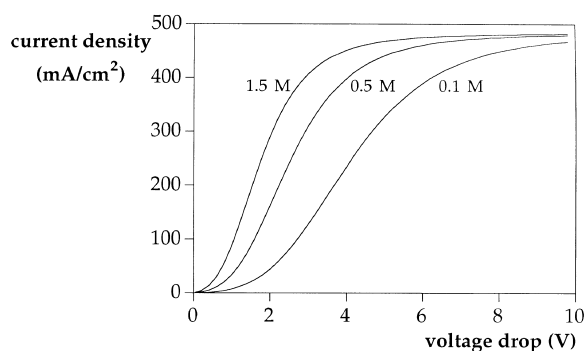


Fig. 14. Calculated current–voltage curves in which the concentration of basic groups at the transition region involved in the water dissociation process is varied. For the calculations a pK_b of 5.0 and a water diffusion coefficient of $5 \times 10^{-10} \text{ m}^2/\text{s}$ was used.

observed that the inflection point shifted to lower current densities (see Fig. 3). If the inflection point in the calculated current–voltage curves is taken as the intercept of the two tangents before and after the inflection, the value of the inflection point is at the same current density for the curves in Fig. 14. This is due to the presence of a true limiting current density in the calculated curves. Thus, a decrease in the concentration of basic groups involved in the water dissociation, as shown in Fig. 14, is not sufficient to obtain qualitative agreement between the calculated and measured current–voltage curves.

The inflection in a calculated current–voltage curve results from a limitation of water supply into the bipolar membrane. As was shown in Fig. 11, a shift in the inflection point to lower current densities can be explained by a reduction in the water diffusion coefficient. A decrease in water diffusion coefficient when the bipolar membrane is damaged can be rationalised by the experimental results with the WSI membrane. The anion exchange layer of the WSI membrane is much thinner than the cation exchange layer. Furthermore, comparison between Table 1 and Table 2 shows that the swelling of the (undamaged) anion exchange layer is higher than the swelling of the cation exchange layer. Therefore, it seems reasonable to assume that the water supply into the bipolar membrane interphase is primarily

determined by the anion exchange layer of the WSI membrane. A lower degree of swelling and a higher area resistance of the anion exchange layer might result in a lower value of the water diffusion coefficient for the damaged bipolar membrane.

4. Conclusions

Current–voltage curves were determined for a Neosepta BP-1 and a WSI bipolar membrane. At higher current density an inflection point is observed at which a sharp increase in the bipolar membrane resistance occurs. Increasing the thickness of the WSI membrane resulted in the inflection point being shifted to lower current densities. This indicated that the inflection point is caused by a limited water supply. Near the inflection point the dissociation of water into protons and hydroxyl ions occurs so fast that the transport of water in the bipolar membrane transition region cannot keep up, the membrane dries out and the resistance increases.

Consecutive current–voltage measurements with the same sample of bipolar membrane were performed up to current densities exceeding the inflection point. The inflection point shifted to lower current densities and the voltage drop shifted to higher values, which indicates that the bipolar membrane resistance has increased. Apparently, the bipolar membrane is damaged irreversibly when applying such high current densities. Experiments with the BP-1 bipolar membrane have shown that the membrane is damaged at current densities well below the inflection point. Two samples of the BP-1 bipolar membrane were pre-treated by either a drying process or exposure to a 0.5 M NaOH solution. Both treatments resulted in a similar change in the current–voltage curve as was obtained when performing consecutive measurements with the same sample of untreated membrane. No conclusions can be drawn as to whether the damage (increase in resistance) is due solely to a drying out of the membrane or to a degradation by alkaline solution (or a combination of both).

The WSI membrane was used to compare the membrane as-received and the membrane that was damaged by applying high current densities. The

properties of the cation exchange layer seemed not to have changed when comparing the damaged and the new membrane. The swelling of the anion exchange layer was found to be lower for the damaged membrane. Simultaneously, an increase in area resistance was measured. This indicates that the amount of fixed charged groups in the anion exchange layer had decreased when the bipolar membrane was damaged by applying high current densities.

Calculated current–voltage curves showed an inflection due to water diffusion limitation, similar to the curves obtained experimentally. It was shown that the location of the inflection point was determined by water transport into the bipolar membrane interphase; a decrease in membrane thickness and an increase in water diffusion coefficient both resulting in the inflection point shift to higher current densities.

The change in current–voltage curve when a bipolar membrane sample is measured consecutive times and damaged could be described qualitatively when it was assumed that both the water diffusion coefficient and the concentration of basic groups involved in the water dissociation reaction had decreased. A decrease in the water diffusion coefficient can be related to the experimental result with the WSI membrane. The decrease in basic groups at the transition region can be rationalised by the measured decrease in swelling and increase in area resistance of the anion exchange layer, which indicate a reduction in the amount of fixed charges in this layer.

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