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Current-voltage curve of a bipolar membrane at high current density

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Abstract

The potential drop across a bipolar membrane was measured as a function of the applied current density. As a result, an inflection point was observed in the obtained current-voltage curve at high current density. This inflection point indicates that at high current densities water supply from outside of the bipolar membrane to the interface between a cation and an anion exchange layer is the rate limiting step for the water dissociation process. The dependence of the current-voltage curve on external conditions such as temperature and feed solution concentration was also investigated. The position of the inflection point changed with the temperature and the concentration of the external solution.

Keywords: Bipolar membrane; Water splitting membrane; Characterization; Membrane resistance

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1. Introduction

A bipolar membrane composed of a cation and an anion exchange layer has unique electrochemical properties which result in the accelerated dissociation of water, i.e. generation of protons and hydroxyl ions, when a high electric field is established across the membrane. This water splitting function of bipolar membranes can be utilized for the production of an acid and a base from a corresponding salt in combination with conventional monopolar ion exchange membranes. Some technically interesting applications with bipolar membranes have been proposed [1, 2].

The objective of this study is to characterize the bipolar membranes in order to get further information about the ions and water transport mechanism in a bipolar membrane. For the characterization of the bipolar membrane, a potential drop across the membrane was measured as a function of applied electric current density. From these measurements, a current-voltage curve is obtained. The current-voltage curve reflects the electric property of the membrane and gives some information about the transport mechanism of ions in the membrane

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structure. Up to date, many people have studied the current-voltage curve of bipolar membranes theoretically as well as experimentally. Much attention was paid to current densities of 0 ~ 200 mA/cm^2 [3–6], because this region is very important in rationalizing the water dissociation mechanism. Generally a current density of about 100 mA/cm^2 is applied in the practical operation of electrodialysis with bipolar membranes [1]. In this report, the current-voltage curve was investigated over a wide current density range, i.e. from 0 to about 1,000 mA/cm^2.

A limitation of the water supply into the membrane at high current density should result in an inflection point in the current-voltage curve. At this point the membrane potential drop across a bipolar membrane rises suddenly, because the water supply into the bipolar membrane becomes the rate limiting step for the water dissociation.

Besides the above described fundamental limitation, the electrodialysis with bipolar membrane at high current density is attractive because of improvements in the membrane electrical properties. In general the electric current efficiency increases with increasing applied current density [7, 8]. The high current efficiency of a bipolar membrane improves the total effectiveness of the electrodialysis system in obtaining high quality concentrated acids and bases. Therefore to investigate the performance of bipolar membrane at high current density is of great practical relevance.

In the present work, the current-voltage curve of a bipolar membrane is determined and the causes and consequences of the inflection point in the curve at high current density are discussed. In addition, the effects of the temperature and the concentrations of the external solutions on the inflection point are investigated.

2. Experimental

The membrane used in this study were a Neosepta BP-1 bipolar membrane, a Neosepta CL-25T cation exchange membrane and a Neosepta ACM anion exchange membrane.

The current-voltage curves were determined by using a test cell as shown in Fig. 1. This cell consists of acid, base, salt and electrode rinse compartments arranged between nickel cathode and platinum anode. The two electrode rinse compartments at the both sides of the cell were separated from the adjacent salt compartments by cation exchange membranes and rinsed with a 0.25 mol/dm^3 Na_2SO_4 solution to avoid penetration of chloride ions to the anode. The effective membrane area of the bipolar membrane and the other membranes were 0.785 cm^2 and 23.76 cm^2, respectively. The membrane area of the bipolar membrane was reduced by means of putting the membrane between two glass plates with a circular hole of 0.785 cm^2 at the centre. A thin rubber sheet was inserted between a membrane and a glass plate. Compared with the bipolar membrane, the other membranes have large membrane areas in order to prevent water dissociation occurring on the surface of these membranes due to the concentration polarization effects.

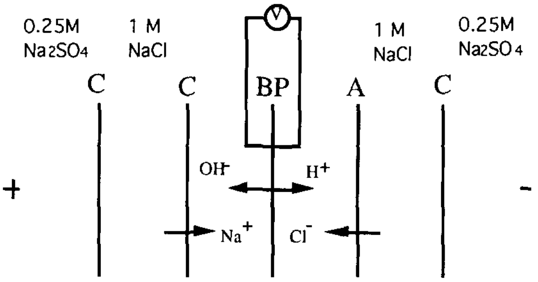

Fig. 1. Cell arrangement for measuring the membrane potential drop across a bipolar membrane. Here are: BP bipolar membrane, A anion exchange membrane and C cation exchange membrane, respectively.

Before the actual experiment, all compartments were filled with the corresponding solutions for a couple of hours to reach an equilibrium state between the membrane and the solutions.

Then the individual solutions were renewed and the measurement was started by establishing an electric field between the electrodes. The potential drop across the bipolar membrane was measured by using two calomel electrodes connected to Haber-Luggin capillaries filled with 1 mol/dm^3 KCl solutions as salt bridge. The edge of two capillaries was set as close as possible to the membrane surface to exclude the influence of the solution between the capillary and the membrane. The temperature of the acid and base solutions was controlled by the thermostated coiled glass heat exchanger placed between the solution reservoir and the cell. The temperature was measured in the reservoir for acid and base solutions. The various cell compartments were supplied with the proper solutions from the reservoirs by peristaltic pumps. In this experiment, 1 mol/dm^3 NaCl and 0.25 mol/dm^3 Na_2SO_4 were used for the salt and electrode rinse solutions respectively. The volume of each solution was about 500 ml for the acid and base, and about 1,000 ml for salt and electrode rinse solutions.

3. Results and discussion

3.1. Current-voltage curves of a bipolar membrane and a cation exchange membrane

Fig. 2 shows the current-voltage curves of a bipolar membrane and a cation exchange membrane. The curves were obtained under the same experimental condition. The potential drop across the bipolar membrane increases rapidly from 0 to about 0.8 V when water dissociation begins in the membrane. After that the membrane potential drop increases linearly with increasing current density up to around 350–370 mA/cm^2. When the current density exceeds this value, the slope changes sharply. It is assumed that this inflection point indicates the rate limiting step of water transport from the outside to the inside of the bipolar membrane. At this point, the water transport into the membrane can no longer meet the water consumption due to the dissociation. However, the change of the slope of the curve doesn't mean that at this point water is completely depleted at the interface where water dissociation occurs. Its concentration is only very low and limit the numbers of protons and hydroxyl ions that can be generated at a given electric field density.

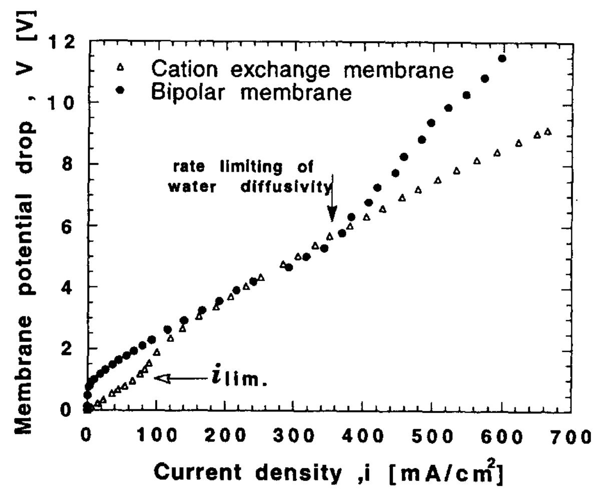

Fig. 2. Current voltage curve of a bipolar membrane and a cation exchange membrane. Initial solutions in acid and base compartments are 0.5 mol/dm^3 NaCl and the temperature of measurement is 20°C.

On the other hand, a change in the slope of the current-voltage curve of a cation exchange membrane is observed around 100 mA/cm^2. This point is known as a limiting current density which is a result of depletion of salt ions due to concentration polarization at the surface of an ion exchange membrane and indicates the beginning of the accelerated water dissociation. The examined monopolar membrane is a normal cation exchange membrane, Neosepta CL-25T. A similar result on the limiting current density of this membrane was reported in the literature [9]. After the sharp increase of the resistance due to the limiting current density, the membrane potential increases linearly and a further inflection point is not observed at higher current densities up to 700 mA/cm^2.

3.2. Membrane resistance (V/i) curves of bipolar and cation exchange membranes

Fig. 3 shows the current density versus V/i curve which is derived from the relationship between membrane potential drop and current density. The membrane potential drop divided by the current density corresponds to the membrane resistance. The bipolar membrane has a minimum value for the membrane resistance around 350~370 mA/cm^2 (point B in Fig. 3). An increase of the current density beyond the point B, leads to an increase in the membrane resistance. The increase of the membrane resistance is assumed to be the results of a decrease in water concentration at the interface between the cation and anion exchange layer. The decrease of water concentration in the membrane reduces the swelling of the membrane and affects the mobility and generation of protons and hydroxyl ions, due to increasing of the frictional resistance for ions transport in the membrane.

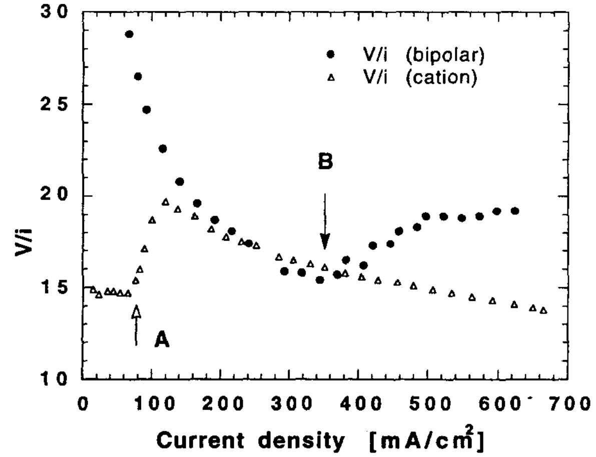

Fig. 3. Membrane resistance (V/i) curve of a bipolar membrane and a cation exchange membrane. Initial solutions in the acid and base are 0.5 mol/dm^3 NaCl and the temperature of the measurement is 20°C.

It is worth noticing that at high current density the increase in the membrane resistance was observed only with the bipolar membrane and not with a cation exchange membrane. This phenomena is an important characteristic of bipolar membranes, which supports the hypothesis that the water diffusivity into the membrane is the rate limiting step for the water dissociation. In the case of cation exchange membranes there is no limitation in the water supply, because water dissociation occurs at the membrane surface which is in direct contact with solution in the cell compartment.

As shown in Fig. 3, the resistance of a cation exchange membrane increases suddenly when the limiting current density caused by concentration polarization is exceeded (point A in Fig. 3). It reaches a maximum value and then decreases gradually with further increasing current density. For this decrease of the membrane resistance, two possible explanations could be considered. One is that the generated protons which have a much higher mobility, become more important as the charge carriers. Another reason may be the heat generation which must also be considered. These experiments were carried out at significantly higher current density than in conventional electrodialysis operation thus, generating a significant amount of heat. The electric conductivity of solution increases with increasing temperature, resulting in a decrease of the membrane resistance.

The membrane resistance of the bipolar membrane also decreases after the resistance peak until the point of limited water supply is reached. The reason for the resistance decrease is probably the same as that of the monopolar membrane.

Although it can not be seen in Fig. 3, the bipolar membrane reaches a maximum in its resistance when the water dissociation starts in the membrane. This resistance peak is much higher than that observed with the cation exchange membrane with the beginning of the water dissociation due to the concentration polarization effects.

3.3. The effect of temperature on bipolar membrane properties

Fig. 4 shows the effect of temperature on the current-voltage curves determining with a bipolar membrane. 0.5 mol/dm^3 HCl and NaOH were used as a initial solutions for acid and base compartments. The observed inflection point in the current-voltage curve shifts to high current densities with increasing temperature. It is assumed that the water activity as well as the diffusion coefficient increases with increasing temperature and that the water transport into the membrane also increases.

The Arrhenius plot of the current density of the inflection point is shown in Fig. 5 for temperatures in the range of 10–50°C. It can be seen that the plots can be represented by a curve with an increasing slope at low temperatures. The activation energy calculated from the slopes of these lines are 2.7 kcal/mol for 20–50°C and 6.4 kcal/mol for 10–20°C. The activation energy at low temperature tends to be higher. A possible explanation for this observation would be that the decrease in temperature reduces the rate of water dissociation in the membrane. It suggests that the inflection point at low temperature is affected by the limitation of the water dissociation rate in addition with the limitation of water supply. The value of the calculated activation energy is depended on the kind of membranes studied. R. Simons also reported an activation energy of 5±1 Kcal/mol to the water diffusion, measured by using labelled isotope [10].

3.4. The effect of the concentration of the external solutions on bipolar membrane properties

Table 1 shows the effect of the concentration of the external solutions on the inflection point at 20°C. Various concentrations of HCl and NaOH were used for the initial acid and base solutions. The inflection point was observed in all experiments. As shown in Table 1, the inflection point shifts to low current densities with increasing external concentrations. The obtained experimental data can be rationalized in terms of an osmotic effect. The increasing osmotic pressure in the outside solutions decreases the water supply into the membrane.

The current density for the inflection point is about 170 mA/cm^2 when the concentration

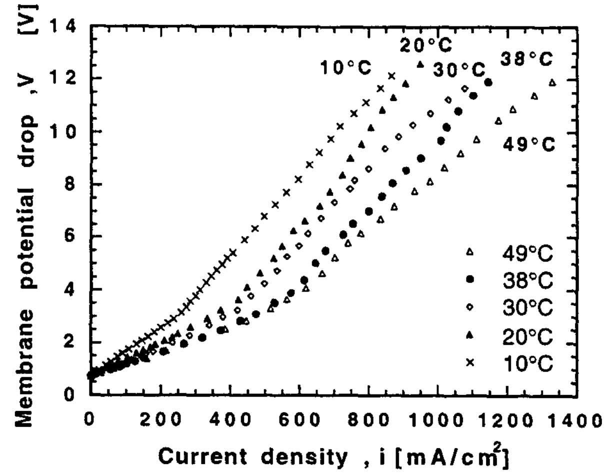

Fig. 4. Temperature dependence of the inflection point in the current-voltage curve. Initial acid and base concentrations are 0.5 mol/dm^3 HCl and NaOH.

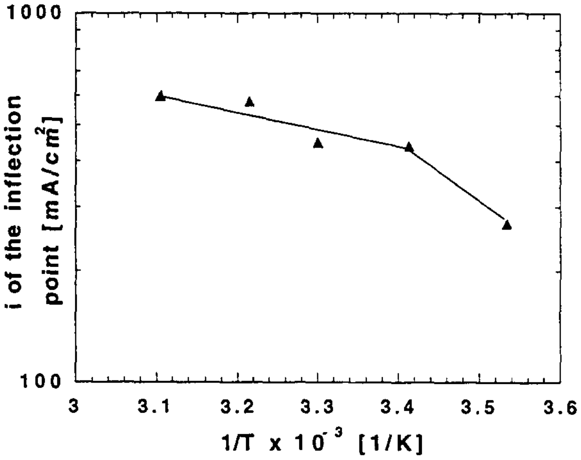

Fig. 5. Arrhenius plot of the current density of the inflection point. Initial acid and base concentrations are 0.5 mol/dm^3 HCl and NaOH.

Table 1
The water consumption due to water dissociation calculated from the inflection points in the current-voltage curves of a bipolar membrane. External solutions are HCl and NaOH at 20°C.

External concentration (mol/l)	0.5	1	2	4	6
Current density of inflection point (A/cm^2)	0.44	0.42	0.36	0.24	0.17
Consumed water [J_{water}] (g/m^2 h)	5,900	5,600	4,800	3,200	2,300

in the outside solutions is 6 mol/dm^3 HCl and NaOH respectively. Compared to an inflection point at 440 mA/cm^2 obtained with outside solution of 0.5 mol/dm^3, the inflection point appears at very low current density. This result also supports the hypothesis that the inflection points are not due to the limitation of water dissociation rate but due to the limitation of water transport, which strongly depends on the osmotic pressure of the outside solutions.

The amount of water dissociation at the inflection point is also listed in table 1. This water amount was calculated roughly from the data of the inflection point by assuming that all electric current is carried by the generated protons and hydroxyl ions. In fact co-ions such as Na^+ and Cl^- permeate also through the bipolar membrane, however, the current density of the inflection point is so high that we can neglect the co-ion leakage in this rough estimation. The estimated amount of water dissociation indicates that the water is supplied from both sides of the bipolar membrane.

4. Conclusions

An inflection point, i.e. a sharp change in the membrane resistance can be observed in the current-voltage curve measured a bipolar membrane at high current density. The inflection point in the current-voltage curve depends on the temperature and the concentration of external solutions. It is assumed that the inflection point is caused by limitation of the water transport into the bipolar membrane.

Acknowledgement

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