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Influence of water content on properties of a heterogeneous bipolar membrane

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ABSTRACT

The heterogeneous ion-exchange membranes consist of polymer matrix and ion-exchange resin powder. The goal of this work was to compare two types of the heterogeneous bipolar membranes made of powdered ion-exchange resin with different water content. The water content influences the resistance of layers and the kinetics of water dissociation. The properties of heterogeneous bipolar ion-exchange membranes were compared due to the current–voltage curve. The evaluated parameters are the limiting current density, the efficiency of the water dissociation, and the resistance below the potential for water splitting. Finally, the bipolar membranes were tested in the electrodialysis stack. The membranes with higher water content had about 25% higher performance at the stack.

Keywords: Heterogeneous bipolar membrane; Ion-exchange resin; Current–voltage curve; Electrodialysis

1. Introduction

The bipolar membrane is ion-exchange membrane consisting of two layers with opposite charges—cation-selective and anion-selective membranes. The theory of bipolar membranes uses the term water splitting which means intensive dissociation of water between cationic-selective layer and anionic-selective layer. Then the protons are transported by the membrane with the acid groups to cathode and the hydroxide ions are transported by the layer with the basic groups to anode. The ion-selective membranes may be heterogeneous or homogenous [1].

The heterogeneous membranes consist of inert binder (i.e. polyethylene) embedding ion-exchange particles. The amount of water contained in the ion-exchange resin significantly affects ion transport across heterogeneous membrane. Regarding bipolar membranes (BM), water is split (i.e. effectively dissociated) in the transition region between cationic-selective layer and anionic-selective layer. The transport of the water to the boundary layer affects the dissociation of the water (Fig. 1). The aim of this work is to verify the

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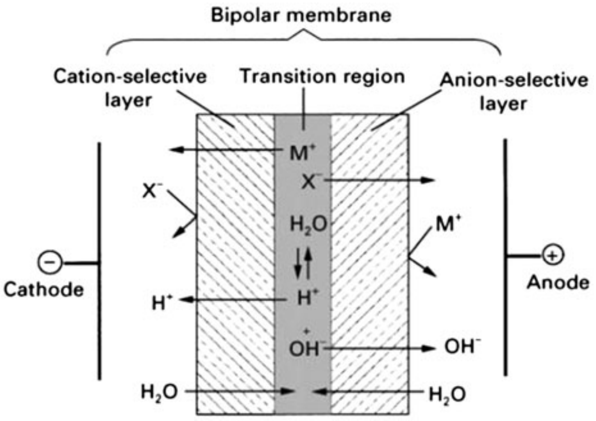

Fig. 1. Processes occurring in the bipolar membrane water splitting operation [3].

influence of water content in the bipolar membranes on their properties. Properties of the bipolar membranes were determined from measurements of current–voltage curves [2]. Samples of bipolar membranes were also tested at the electrodialysis stack EDBM-Z.

2. Experimental

2.1. Preparation of bipolar membranes

The samples of BM were prepared from two batches of cation-exchange resin and two batches of anion-exchange resin. The sample BM1 contains the resins with higher water content and the sample BM2 contains the resins having lower water content. Properties of the ion-exchange resin and the composition of the samples are presented in the Table 1.

The selected ion-exchange resins were dried and powdered in the vibratory mill. The three parts of ion-exchange resin were homogenized with two parts of polyethylene matrix. The samples of bipolar membranes were produced on a co-extrusion line. Both samples of bipolar membranes were treated under the same conditions.

Table 1
Samples composition

Sample	Resin	Water content (%)	IEC (eq/l)
BM1	Anion exchange	63	0.8
	Cation exchange	58	1.6
BM2	Anion exchange	52	1.3
	Cation exchange	50	1.9

2.2. Current–voltage curves

BMs swelled in the demineralized water and then were converted to the correct ionic form in 0.25 M K_2SO_4 solution. Current–voltage curves were determined by the four-electrode technique using the conical-shaped cells to make the current approximately homogeneous (Fig. 2). The bipolar membranes were measured at 25°C in 0.25 M K_2SO_4 solution. The effective cross-sectional area of membrane was 0.74 cm^2. The curve was measured until the current was increasing in time due to the dry-out effect [4].

2.3. Process tests at the electrodialysis stack

Both types of the bipolar membranes were tested in the laboratory unit EDBM-Z/3-0.8. The aim of this test is to simulate the conditions of the real process and monitor the behavior of membranes in response to these conditions. The test parameters are in the Table 2.

The voltage, current, temperatures, conductivities, and pH of all solutions were recorded during the demineralization. From these measured data were determined the efficiency of the process, the mass flow of salt, and the energy consumption for the transport of salts. All calculated values were related to 90% of demineralization.

Current efficiency η (%) based on the amount of dissociated Na_2SO_4 was determined according to Eq. (1).

$$\eta = \frac{v \cdot z \cdot F \cdot \Delta n}{N \cdot Q} \cdot 100\% \qquad (1)$$

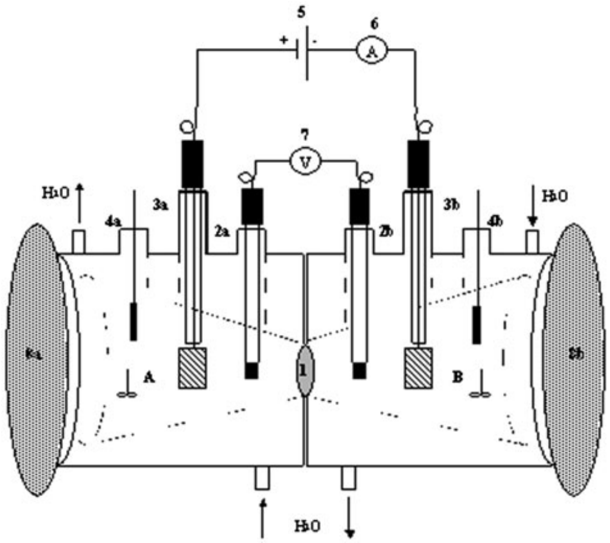

Fig. 2. Scheme of measuring cell [5].

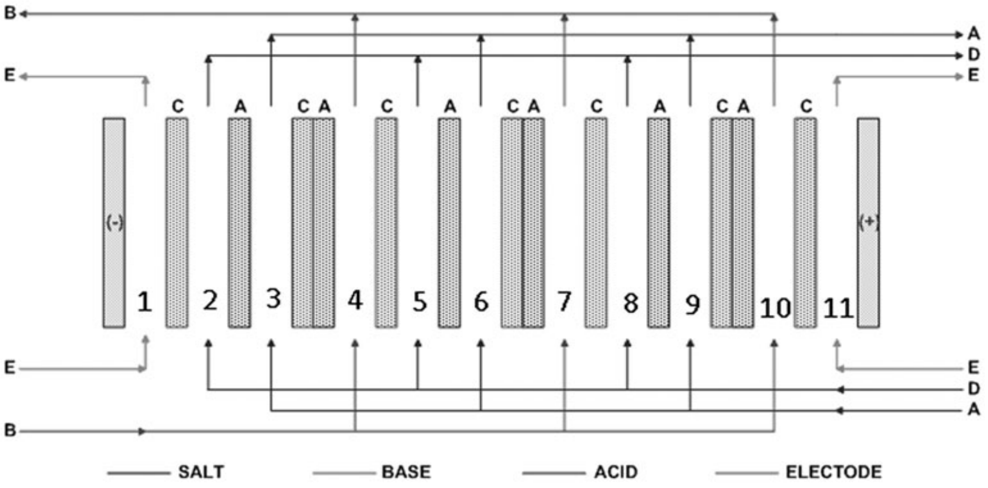

Fig. 3. Schema of a stack.

Table 2
Parameters of EDBM tests

Composition	– CM_AM_BM_CM_AM_BM_CM_AM_BM_CM +
Salt loop (S)	Na_2SO_4; volume 0.6 l; concentration 10 g/l
Acid (A), Base (B) loops	0.3 l demineralized water
Electrode loop (E)	Na_2SO_4; volume 0.3 l; concentration 10 g/l
Flow rate S, A, B	20 l/h
Flow rate E	50 l/h
Voltage	3 V/BM (9 V/stack)
Effective area of BM	192 cm^2
Total installed area of membranes	1153.6 cm^2
End of the test	90% demineralization of S
Spacer thickness	0.8 mm

v – stoichiometric coefficient; z – valence of the ions; F – Faraday constant; Δn – amount of the decomposed Na_2SO_4; N – number of BM; and Q – electric charge.

The mass flow of salt J ($g/m^2 \cdot h$) was determined according to Eq. (2).

$$J = \frac{\Delta m}{A \cdot \Delta t} = \frac{\Delta m}{N \cdot w \cdot l \cdot \Delta t} \qquad (2)$$

Δm - weight of the decomposed Na_2SO_4; A – effective membrane area; N – number of BMs; w – the effective width of the membrane; l – the effective length of the membrane; and t – test period.

Specific energy consumption E (Wh/kg) per 1 kg decomposed Na_2SO_4 was determined according to Eq. (3).

$$E = \frac{U \cdot Q}{\Delta m} \qquad (3)$$

U – voltage; Q – electric charge; and Δm – weight of the decomposed Na_2SO_4.

3. Results

The current–voltage curves of both BMs samples can be seen in the graph (Fig. 4). The experimental data were smoothed by the functions. The limiting current densities were calculated from the explicit expression of these functions. The limiting current density of sample BM1 (resin with high water content) is $I = 198.9\ mA/cm^2$ and the limiting current density of the sample BM2 (resin having a lower water content) is $I = 188.1\ mA/cm^2$. The slopes of both curves are identical at the voltage lower than 4 V. Over this value, the difference between two samples becomes higher. The origin point of water dissociation in the graph does not reveal.

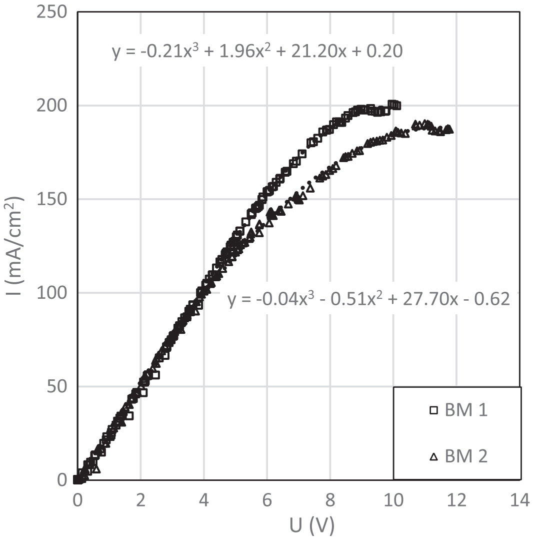

Fig. 4. Current–voltage curves.

The samples of bipolar membranes (BM1 and BM2) were tested at the electrodialysis stack EDBM-Z/3-0.8. The decomposition of sodium sulfate to sulfuric acid and sodium hydroxide is shown in the graph (Fig. 5). There is a noticeable difference between the samples of BM.

The parameters calculated by the above Eqs. (1), (2), and (3) are shown in Table 3. These values are average from results of four tests.

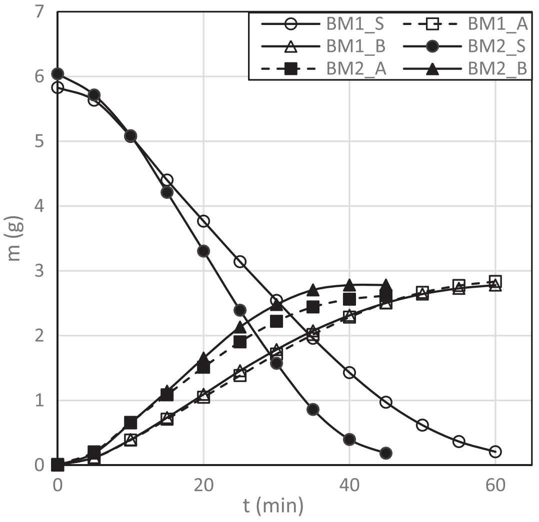

Fig. 5. Process of decomposition of sodium sulfate. S – salt, A – acid, B – base.

Table 3
Average results of tests

Sample	η (%)	E (W h/kg)	J (g/h m^2)
BM1	81.4	1391.1	372.0
BM2	63.6	1786.1	270.3

4. Conclusion

The current–voltage curves shows that the difference between the bipolar membranes is significant at higher voltages only. The amount of water in the membrane influences the kinetics of water dissociation only at a higher voltage. It has a major influence on the limiting current density.

Comparing the performance of both samples in the laboratory stack EDBM-Z shows that the membranes containing ion-exchange resin with higher water content have 25% higher performance.

The voltage is less than 3 V per one BM in the stack. That corresponds to the region of current–voltage curves where the membranes should have the same performance. It is obvious that the process of dissociation of salts depends on further parameters.

Acknowledgments

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