Heterogeneous bipolar membranes and their application in electrodialysis

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HIGHLIGHTS

- A complex of data regarding heterogeneous BPM investigation is presented.
- Aspects of BPM structure, water splitting and ion transfer mechanisms are revealed.
- Operating parameters of BMED in novel electromembrane processes were investigated.
- Heterogeneous BPMs can be applied in novel electrodialysis applications.

ARTICLE INFO

ABSTRACT

Over the last 50 years, ion exchange membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impacts. Bipolar membranes (BPMs), as a result of their ability to produce acid and alkali from corresponding salt, occupy a special place among them. These properties make it possible to design a number of unique electromembrane processes which have huge industrial impact. These processes include acid and base syntheses, electrochemical regeneration of acidic and basic gas sorbents and ion-exchange resins, protein separation and pH correction of natural waters and juices. The main characteristics that define the possibility of effective BPM application are total potential drop across the membrane and water dissociation current efficiency. These two parameters are closely related to each other and determined by the physical and chemical structures of monopolar layers and the nature of the water dissociation reaction catalyst located in the bipolar region. In this particular article the electrochemical properties of heterogeneous bipolar membranes, methods for investigating them and various theories developed to describe water dissociation are discussed. Comparison between Russian industrial heterogeneous bipolar membranes and various commercial and experimental foreign bipolar membranes is made. In addition, some novel electromembrane processes developed for application of heterogeneous bipolar membranes and their main characteristics are presented.

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List of symbols

Symbol		Dimension
T_i	Effective transport number of ion	
t_i^M	Electromigration transport number of ion	
P_i	Diffusive permeability of the membrane to ion	$mol/(cm^2 \cdot s)$
Δc_i	Concentration difference on the inlet and outlet of electrochemical cell for ion	mol/L
F	Faraday constant	$A \cdot s/mol$
i	Current density	mA/cm^2
S	Membrane active area	cm^2
I	Current, applied to the cell	A
w	Volume flow rate of solution	L/s
R_b	Resistance of the reaction layer	$\Omega \cdot cm^2$
R_0	Real part of impedance at low frequency	$\Omega \cdot cm^2$
R_∞	Real part of impedance at high frequency	$\Omega \cdot cm^2$
η_b	Bipolar region overvoltage	V

(continued)

Symbol		Dimension
U_{tot}	Voltage drop on membrane	V
U_0	Voltage drop on monopolar layers of bipolar membrane	V
N_+, N_-	Ion-exchange capacity of anion- and cation-exchange layers	mol/L
l	Thickness of the reaction zone inside the BPR where water splitting occurs	m
ε	Relative dielectric constant of the space charge region	
ε_0	Absolute permittivity of the vacuum	F/m
C_{sp}	Electric capacity of the space charge region	F
k_d	Water molecule dissociation rate constant in the electric field with electric field strength E	1/s
$k_d(0)$	Water molecule dissociation rate constant in the absence of electric field	1/s
β	Entropy factor	m/V
k_Σ	Total effective water dissociation rate constant in the space charge region in the absence of an electric field	1/s
E_m	Electric field at the interface between CEL and AEL	V/m
E_0	Electric field at zero bipolar region overvoltage	V/m
$C_{H+}{}^c, C_{H+}{}^a$	Concentration of hydrogen in CEL and AEL	mol/L

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Symbol		Dimension
η	Current efficiency	
V	Treated solution volume	L
W	Specific energy consumption	kW·h/kg
$U_{el, cell}$	Voltage drop across elementary cell of electrodialysis module	V
P	Specific production rate	kg/(m^2·year)

1. Introduction

Bipolar membranes (BPMs) are bilayer composites, in which cation- (CEL) and anion-exchange (AEL) layers possess ion-selective properties (Fig. 1). Bipolar membranes occupy a special place among ion-exchange membranes due to their ability to generate protons and hydroxyl ions from water molecules under direct current polarization. Water dissociation occurs in the bipolar region (the place where CEL and AEL are conjoined) of the BPM only when its cation-exchange layer faces the cathode and the anion-exchange layer faces the anode and electric current is passing through the membrane (the so-called generation mode).

This type of ion-exchange membrane was referred to for the first time in an article by Frilette [1] published in 1956. Intensive study of the properties of bipolar membranes began in the 1950s–1970s: the study of acid and alkali production by BPMs [2–4], as well as the study of salt ion transport through the membrane [5,6]. The publication of Mauro's [7] article, in which the theory developed for the *p–n* junction in semiconductors was applied to the space–charge region in the bipolar membrane, marked the beginning of the modern theoretical study of bipolar membranes. In addition, some interest was given to ways of creating ionic analogs of the semiconductor diode and transistor electronic devices [8–10]. It was found that the asymmetry of the bipolar membrane can separate ions with the same sign but with different absolute values of the electric charge [11] and that the potential difference across the bipolar membrane depends on not only the density of the electric current [1], but also the pressure difference across the membrane [12] and the intensity of the light flux incident on the BPM [13]. Even in these early studies, it was found that the nature of the electrolyte solution affected BPM properties [14]. The emergence of the first bipolar membranes coincided with increased interest in biophysical studies of biological membranes in the 1950s and 60s. At this time, it was shown that some electrical properties of biological membranes, in particular their current–voltage characteristics [15], could be explained by the existence within them of layers of fixed ions such as those in ion-exchange bipolar membranes with different electric charge signs.

By the early 1970s the main fields of application for bipolar membranes were processes that use their ability to generate hydrogen and
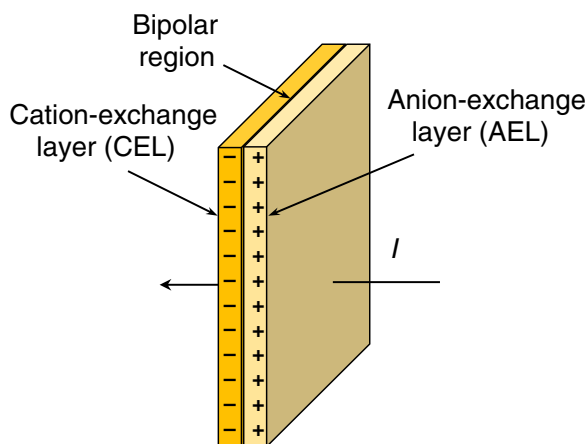

Fig. 1. Diagram of a bipolar membrane showing the orientation of the electric current vector.

hydroxyl ions by passing an electric current through the membrane. Other uses of bipolar membranes did not appear as promising as ionic analogs of diode and transistor can only be used at low frequencies (below 0.1 Hz) due to the mobility of hydrogen and hydroxyl ions in the cation and anion-exchange membrane layers being approximately three orders of magnitude less than the mobility of electrons and holes in the silicon and germanium. Biological membranes, as have been shown in subsequent years, have a more complex structure and variety of ion transport mechanisms than bipolar ion exchange membranes, and therefore in this case the analogy is not complete. At the same time, the ability of bipolar membranes to separate one-, two- and three charged ions has been further developed to create charge selective membranes [16]. Use of bipolar membranes as a proton-conducting material in methanol fuel cells also looked promising [17].

In the 1970s the first industrial bipolar membranes were created in Russia [18], Japan and the USA [19–24]. Since that time, Russia, as well as the USA, Japan, Europe, and Australia, and in recent decades China [17,25–30] and South Korea [31–35] have been developing bipolar membranes, studying their characteristics and developing processes based on the use of bipolar membranes.

The most important achievement of the period of research beginning in the 1970s is the understanding of the mechanism of water molecule dissociation in the bipolar membranes, providing a dissociation rate many orders of magnitude greater than in pure water [36–46]. It should be noted that the same mechanism applies to the cation-exchange membrane/solution and the anion-exchange membrane/solution interfaces. It has been firmly established that the reaction of water dissociation in bipolar membranes occurs according to the catalytic mechanism of direct participation of fixed ionogenic groups [36,47] or specific organic [24,48–52], and/or inorganic [53–59] additives introduced into the bipolar region (BPR). In addition, the rate constant of water molecule dissociation in the BPR increases with an increase in the electric field strength within it with an increase in current density as a result of polarization of the bond in the water molecule, and a weakening of the bond in the external electric field [41,42], or as a result of acceleration of proton transfer in the chains of favorably oriented water molecules (a cooperative proton transfer) under the influence of the electric field [39,43]. The rate of water dissociation outside the BPM space–charge region reaction layer was found to be negligible. This mechanism means the water dissociation reaction in bipolar membranes can be considered to be electrocatalytic, and the BPMs themselves to be specific electrochemical nanoreactors.

In recent years, electrodialysis with bipolar membranes (BMED) has been widely used to produce ultrapure deionized water [60] and for deep cleaning of organic and inorganic substances in the chemical and biochemical industries, production of organic and inorganic acids and bases from the respective salts [61–74], in the food industry to separate organic acids from solutions formed in the enzymatic processes [75–77], for pH correction of fruit juice [78–81], whey protein [82,83], whey formed in processing cheese and soybean [84–87] and other products [88–92], and pH correction processes in chemical solutions [93,94]. Recently researchers have shown increasing interest in electrodialysis processing of solutions containing organic components such as methanol, ethanol, 1-propanol, ethylene glycol and propylene glycol [95], preparation of sodium methoxide [96] of methoxyacetic acid, methyl ester [97], acetoacetic ester [98,99], and methyl ester of palmitic acid [100], to carry out chemical reactions such as the Claisen condensation and the intramolecular Dieckmann condensation reactions [17], and the use of bipolar membranes in hydrometallurgy, in combination with electrolysis (electro-electrodialysis processes) [101], as well as membrane reactors [102]. Asymmetric bipolar membranes, in which the thickness of the monopolar layers differs significantly, make it possible not only to change the pH of solutions due to the generation of acids and alkalis, but at the same time also to desalinate them [103–107]. Studies of electrochemical properties of BPMs and electromembrane