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An investigation through the validation of the electrochemical methods used for bipolar membranes characterization

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ABSTRACT

Four types of bipolar membranes (BMs) with different structural properties were subjected to various electrochemical methods including current-voltage curve, (CVC) chronopotentiometry, and impedance spectroscopy, to be characterized in terms of selectivity, energy consumption and the water splitting capability. Then the bipolar membranes were used in two kinds of electrodialysis modules, lab scale and pilot unit, for acid and base production. The produced acid and base were analyzed to calculate the product purity, energy consumption and current efficiency of each bipolar membrane electrodialysis (BMED). The results obtained with electrodialysis coincided with those of electrochemical methods, indicating that even though the electrochemical methods are rather fast and easy to perform, they are quite reliable. Furthermore the impact of structural properties of each BM on its efficiency was investigated. It was figured out that the reinforcing of a heterogeneous BM improves its properties while the increase in the ion exchange resin content on each layer of the heterogeneous BMs was not resulted in any significant enhancement of BM properties. The investigated homogenous membrane showed higher selectivity and less energy consumption compared to the heterogeneous BMs.

1. Introduction

Bipolar membrane electrodialysis (BMED) has found a wide range of applications in industries due to its features. Currently, BMED is applied in diverse areas such as waste water treatment [1], producing acid and base from the salt stream, recovery the concentrated acid [2–6], pharmaceutical industries [7] food industries [8–13].

Regarding the structure, a bipolar membrane BM involves two ionic exchange layers with opposite fixed charge joined together in series. The characteristics of the BM such as ionic selectivity and particularly electric field enhanced (EFE) water splitting as its most prominent features stem from its particular arrangement. The EFE water splitting starts at bipolar interface when a sufficient dc current is directed through the bipolar interface under reverse polarization [14–19].

The BMED for producing acid and base from a salt stream involves a membrane arrangement so-called three-compartment stack. To briefly explain, the acid, salt and base compartments which are confined by a BM together with a pair of cation and anion permeable membranes form the repeat unit. The acid and base are produced, when the salts stream's anions and cations transport through the anion and cation exchange membranes and are respectively combined with the proton and hydroxide ions generated at bipolar interface. Hence, the acid and base production is achieved with a pair of electrodes and many repeat units in between, resulted in a lowered cost and the reduced influence of the electrode reactions [20].

Thus, the efficiency of the BMED depends on water splitting at bipolar interface which is further considered as an electric field-enhanced (EFE) phenomenon and its value crucially relies on structure and composition of the bipolar interface [21,22]. Moreover the purity of the generated products (acid and base) is mainly determined by the salt ion transport across the BM [23].

Accordingly the BMs must be characterized in terms of energy consumption (electrical resistance and water splitting capability), product purity (selectivity toward counter ion), water permeability of the monopolar layers, and the chemical stability. Therefore, advanced characterization methods are desired to improve the material of a BM and its transport properties to overcome existing limitations such as low selectivity or high energy consumption.

Among various methods used for the BMs characterization the electrochemical techniques including membrane potential [24,25], current–voltage curve (CVC), I–V. [15–18,26,27], Chronopotentiometry [20,23], impedance spectroscopy [22–28] provide valuable information about the functional and structural characteristics of BMs. Furthermore, the electrochemical techniques are easy to perform

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Nomenclature

A/m^2	Membrane geometric surface area
A_{ef}/m^2	The contact effective area of interface boundary
C/F	Equivalent capacitance
$\overline{C}_{m,0}$/M	Initial virtual salt concentration at time t_0 in the BM layers
C_f/M	Final concentration
C_{co}/M	Initial co-ion concentration at time t_0 in the BM layers
C_{count}/M	Initial counter-ion concentration at time t_0 in the BM layers
$D_{av,m}/m^2\,s^{-1}$	Average apparent diffusion coefficient of the electrolyte
$D_{co}/m^2\,s^{-1}$	Average apparent diffusion coefficient of the co-ion
$D_{count}/m^2\,s^{-1}$	Average apparent diffusion coefficient of the counter-ion
E_{conc}/V	Potential resulted because of concentration gradient across the membrane layers
E_{react}/V	Potential resulted because of chemical reaction across the membrane layers
$F/96{,}485\ C\,mol^{-1}$	Faraday constant
G/Ω^{-1}	Equivalent conductance
Im(Z)/Ω	Imaginary part of impedance
$j/A\,cm^{-2}$	Current density
$j_{lim}/A\,cm^{-2}$	Limiting current density
$J/g\,s^{-1}\,m^{-2}$	Mass flux across the membrane
$MW/g\,mol^{-1}$	Molecular weight
Δm/g	The converted mass of the salt
N	Number of the Bipolar membranes in the stack
$Purity_A$%	Purity of the produced acid
$purity_B$%	Purity of the produced base
Q_E/C	The required charge for converting Δm of the salt
ΔQ/C	The consumed charge for converting Δm of the salt
R_b /Ω	The resistivity of the bipolar interface
$Re(Z)/\Omega$	Real part of the impedance
R_0/Ω	The real part of the impedance at low frequency
R_∞/Ω	The real part of the impedance at high frequency
$r_{equilibrium}/\Omega$	The resistivity of the BM in equilibrium state
$r_{transport}/\Omega$	The resistivity of the BM in transport state
t /s	Time
$t_{i,A}$	(Migrational) transport number of the ion i in anion exchange layer
$t_{i,C}$	(Migrational) transport number of the ion i in cation exchange layer
τ_1/s	Transition time
τ_D /s	Discharging time
U /V	Potential
$U_{m,off}$ /V	Switch off potential
$U_{m,irr}$ /V	Irreversible contribution of the $U_{m,\ stat}$
$U_{m,rev}$ /V	Reversible contribution of the $U_{m,\ stat}$
$U_{m,\ stat}$/V	The potential in transport state
U_{tot}/V	Total potential across the BM
U_0/V	The potential drop in monolayers
W /W h	The electrical energy used in EDBM
W'/W h/g	The electrical energy used for converting one gram of the salt
η_b / V	Bipolar interface potential
ω/Hz	Angular Frequency
ν/Hz	frequency
λ/m	The thickness of the bipolar interface
ε_r	Dielectric constant (20 for polymeric membranes)
$\varepsilon_0/8.85\times10^{-12}\,F\,m^{-1}$	Vacuum permittivity
χ /s^{-1}	The effective water splitting rate constant

and rapid which make them convenient to be applied frequently for BM characterization.

Although, there are many researches carried out about the theory behind of each individual of abovementioned techniques, into our best there is not any effort about the validation of these techniques to find out, despite the theory, how reliable the results obtained by electrochemical characterization of the BMs are.

The aim of the current work was to investigate the validity of the electrochemical characterization of BMs. For this purpose four kinds of BMs with different structural properties were subjected to the various electrochemical techniques; CVC, chronopotentiometry and impedance spectroscopy to evaluate them in terms of the selectivity and energy consumption. Then the membranes were also utilized in two sorts of EDBM modules for acid and base production. The first one was lab scale module and the second one was pilot unit (both are described in Sections 4.4 and 4.5). The results of the electrochemical characterization were compared to those of BMED to get insight about the reliability of the results obtained with electrochemical techniques.

2. Theoretical descriptions

2.1. Current voltage curve (CVC)

Bipolar membranes CVC, is composed of three regions (shown in Fig. 1a). The first region (R_1) in which the potential across the membrane increases linearly with the applied current, indicates the BM resistivity. The linear relation of potential upon the applied current could be explained by imperfect selectivity of the monolayers, resulting in migrational transport of some amount of co-ions through the anion and cation exchange sides of the BM. With further increasing the current, the bipolar interface depletes from the transported ions and at a given current density called the limiting current density (j_{lim}), there are no more ions in the bipolar interface to carry the current. Hence the bipolar interface resistivity increases and the potential drop across the BM jumps till a value at which water splitting starts at bipolar interface. The bipolar interface becomes accumulated with water splitting products which are capable of transferring the current. As a result the third

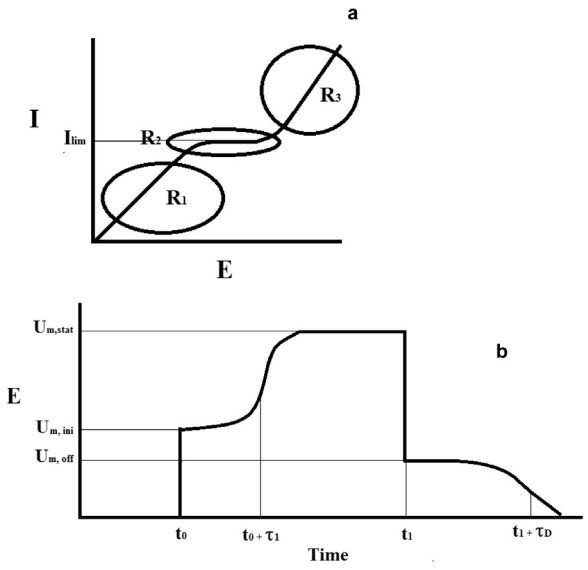

Fig. 1. a; Typical current-voltage curve of a BM, R_1; sub-limiting current region, R_2; limiting current region, and R_3; over-limiting current region. **b**; typical chronopotentiogram of a BM, $U_{m,\ ini}$; the initial increase in potential drop after switching on the current, $U_{m,\ stat}$; potential of across the BM at transport state. $U_{m,\ off}$; potential across the BM after switching off the current, τ_1; transition time, τ_D; discharging time, t_0 and t_1; the times of switching on and switching off the current.