On the drying out of bipolar membranes

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Abstract. The maximum current density that can be achieved in bipolar membrane electrodialysis is limited by the sharp increase in resistance that is experienced when the water content at the membrane interface is not adequately replenished and the membranes dry out. In this paper we show how the water content near the interface depends on the properties of the membranes. A water retaining parameter is introduced, which characterizes the thermodynamic properties of the membrane material and may be used to guide the choice of polymers for mitigation of the dry-out problem.

Keywords: bipolar membrane; dry-out; current-voltage curve; electro-osmosis; water absorption

1. Introduction

Bipolar membranes (BPMs) are a laminate of an anion and a cation selective layer that are firmly bound together. Water is supplied by diffusion to the interface of the ion and cation layers where hydroxide ions and protons are generated by dissociation under an applied electrical field. In BPM electrodialysis, anion, cation and bipolar ion exchange membranes are stacked into a membrane module to produce acids and bases from their corresponding salts. BPM electrodialysis has been implemented in a variety of applications, including the production of inorganic acids and bases, production of organic acids, acid and/or base regeneration and recycling, and for various processes in the agro-food and pharmaceutical industry (Huang and Xu 2006). Despite its potentialities for improving the energy efficiency of conventional industrial processes and their environmental sustainability by reducing release of contaminants to the environment, BPM electrodialysis has met thus far only limited commercial adoption, mainly due to the present limitations of state-of-the-art BPM processes (Xu 2005).

The limited performance in replenishing the water dissociated at the interface between the cation and anion exchange layers is generally acknowledged as one of the principal limitations of BPM processes (Aritomi *et al.* 1996, Balster 2006, Balster *et al.* 2007). In the absence of adequate water transport from the bulk solutions, the BPM interface dries out causing a sharp increase in the electrical resistance. This is reflected in an inflection point in the current-voltage curve with detrimental effects on process performance.

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The rate of water splitting is determined by the intensity of the applied electrical field. Hence avoiding the drying out of BPMs translates into a limitation in the maximum applicable current density. The current density at which drying out occurs depends, among others, on temperature and concentration of the external solutions (Aritomi *et al*. 1996), but in practical applications it is usually assumed that current density should not exceed 200 mA/cm^2 in order to avoid the risk of irreversible damage in the BPMs (Krol *et al*. 1998).

Various approaches have been proposed to enhance water transport to the interface and limit the occurrence of drying out. Balster (2006) introduces a thin layer with a high amount of ionic groups between the cation and anion exchange layers. The addition of highly sulphonated poly (ether ether ketone) to the intermediate layer is found to enhance the water splitting reaction and increase the hydrophilicity and water content of the BPM interface. The study, however, does not investigate the performance of the BPM at current densities higher than 100 mA/cm^2.

This paper analyses the processes and conditions that lead to drying out of BPM. The principal equations governing water flow to the membrane interface are derived (Sections 2-5). Further, we identify and discuss the membrane properties that determine the water content and conditions for dry-out of the BPMs (Section 6-7).

2. Flows and forces in ideal bipolar membranes

When a current is passed through a BPM, water is split at the interface between the cation exchange and the anion exchange membranes. For the present analysis, an ideally selective BPM is assumed, in which the current is carried only by protons and hydroxyl ions, neglecting the influence of the possible small flows of salt ions on water flow.

Considering flows in the cation exchange membrane (CEM) and assuming a symmetric BPM, the current density is given by

$$I = FJ_+ \tag{1}$$

where J_+ is the flow of protons. The depletion of water by dissociation creates a gradient of the thermodynamic potential, μ_w, and a driving force, X_w, for the flow of water from the solutions towards the interface.

$$X_w = -\frac{d\mu_w}{dx} = -V_w\left(\frac{dp}{dx} - \frac{d\pi}{dx}\right) \tag{2}$$

Water flow, J_w, is driven by X_w and dragged along by the ions in electro-osmosis. Water flow is directed towards the interface while ions flow away from the interface.

$$J_w = L_w X_w + \beta\frac{I}{F} = L_w X_w + \beta J_+ \tag{3}$$

The electro-osmotic coefficient β represents the amount of water that would be pulled out from the interface per faraday, i.e., the number of moles of water per mole of protons flowing into the left bulk solution adjacent to the cation exchange membrane when $X_w = 0$.

The local transport coefficient L_w relates the flow to the local gradient and depends on the local properties of the membrane.

3. Correlations in ideal bipolar membranes

In ideal BPMs the flow of water and the current are directly related. All current is carried by ions formed by dissociation of water, and, for symmetric membranes, water flows equally through both membranes. The water flow through the CEM, J_w, is half of the total water supplied to the interface. The proton flow through the CEM contains the protons supplied by water flow through both the CEM and the anion exchange membrane (AEM).

$$\frac{I}{F} = J_+ = -2J_w \tag{4}$$

where both J_+ and J_w are expressed in mol/m sec. Substituting Eq. (4) into Eq. (3), one obtains

$$X_w = -\frac{I}{2FL_w}(1+2\beta) = \frac{J_w}{L_w}(1+2\beta) \tag{5}$$

4. Osmotic pressure in the membrane

For many purposes, it is convenient to treat the membrane as a single phase, containing polymer or polymers, solvent and solutes. However, for an evaluation of the mechanical equilibrium at the interface it is simpler to distinguish between the solid polymer network and the liquid solution that flows in the pores, however small. In the flow of water through pores, driven by the gradient of μ_w, there is transfer of momentum that is balanced by the force holding the porous medium in place, in this case the CEM and AEM holding each other in place.

No external pressure gradient is applied and thus the driving force developed in the water is only the osmotic pressure gradient created by relative depletion of water by the dissociation reaction. Then the driving force for the water is

$$X_w = -\frac{d\mu_w}{dx} = V_w\frac{d\pi}{dx} \tag{6}$$

Introducing Eq. (6) into Eq. (5), the gradient of osmotic pressure can be expressed as a function of the applied current.

$$\frac{d\pi}{dx} = -\frac{I}{2FV_wL_w}(1+2\beta) = \frac{J_w}{V_wL_w}(1+2\beta) \tag{7}$$

With increasing current the osmotic pressure gradient increases, the amount of water relative to polymer decreases at the interface and the permeability decreases. To supply water to the dissociation reaction, the osmotic pressure near the interface further increases, the membrane shrinks and eventually it is blocked, dried out.

In order to obtain an approximate estimate of the osmotic pressure at the interface of a BPM one can assume, just for the sake of the estimate, an average value of L_w independent of concentration. Then the difference in the osmotic pressure measured at the interface, π_i, and in the bulk, π_0, can be calculated as

$$\pi_i - \pi_0 = \frac{J_v}{L_p}(1 + 2\beta) \tag{8}$$

where $J_v = V_w J_w$ is the volume flow of water, Δx is the thickness of the membrane and $L_p = L_w V_w^2 / \Delta x$ is the hydraulic permeability.

Assume a minimal value for the electro-osmotic coefficient of $\beta = 1$. For the proton this means that the hydronium ion is the migrating species (Kreuer *et al.* 2008). At a current density of 200 mA/cm^2, the volume flow in the CEM is given by $J_v = 1.9 \times 10^{-7}$ m/sec. This value can be expressed in the units that are customary in pressure driven processes as $J_v = 0.7$ LMH. The hydraulic permeability was measured for some ion exchange membranes. In particular, Narebska *et al.* (1985) characterized Nafion 120 in great detail and found $L_p = 2 \times 10^{-14}$ m^3/N sec, which is equivalent to $L_p = 7.2 \times 10^{-3}$ LMH/bar.

Hence, from Eq. (8): $\pi_i - \pi_0 = 280$ bar. Such value corresponds to about ten times the osmotic pressure of seawater. This is a very high but still reasonable value in an ion exchange material. Such high osmotic pressures are best expressed as vapor pressure of water, p, where the relation between vapor pressure and osmotic pressure is given by

$$\pi V_w = RT \ln \frac{p_0}{p_s} \tag{9}$$

where p_0 and p_s are the partial vapor pressures of pure water and of a solution. At room temperature, $RT/V_w = 1385$ bar, hence at an osmotic pressure of 280 bar the vapor pressure of water will be reduced by approximately 20%.

5. The concentration dependence of the local transport coefficient L_w

In order to understand the relation between the structure of ion exchange membranes and their function, it is necessary to distinguish between the thermodynamic interaction between membrane polymer, water and ions and the friction between these species. The local transport equations can be derived from the force balance (Spiegler 1958, Kedem and Freger 2008).

At every point in the membrane there is local mechanical equilibrium. The driving force per mole of species i is balanced by the friction between one mole of i and all molecules in the surrounding medium.

$$-\frac{d\widetilde{\mu}_i}{dx} = \sum F_{ij} = \sum f_{ij}(v_i - v_j) \tag{10}$$

where f_{ij} is the friction between one mole of i and molecules of j in the surrounding medium and the term $v_i - v_j$ is the relative velocity of species i with respect to j. For water in the CEM

$$X_w = f_{wm}v_w + f_{w+}(v_w - v_+) = (f_{wm} + f_{w+})v_w - f_{w+}v_+ \tag{11}$$

The coefficient f_{wm} refers to friction between water and the polymer constituting the ion exchange membrane without its counterions, and the polymer is taken as the reference so that the velocity of the polymer is zero.

Substituting in Eq. (11) the general relation between flow and velocity

$$J_i = v_i C_i \tag{12}$$

$$J_w = \frac{C_w}{f_{wm} + f_{w+}} X_w + \frac{f_{w+} C_w}{(f_{wm} + f_{w+}) C_+} J_+ \tag{13}$$

where C_w and C_+ are the concentrations of water and protons per unit volume of the membrane phase.
Comparison of Eq. (3) and Eq. (13) shows that.

$$L_w = \frac{C_w}{f_{wm} + f_{w+}} \tag{14}$$

Following Eq. (14), the coefficient L_w is expected to depend on the concentration of water in the membrane both directly and indirectly, through a possible concentration dependence of the frictions coefficients. Without a specific model it is reasonable to assume that with decreasing water content and thus narrower channels between the polymer chains the friction between water and polymer will increase.

6. Conditions for dry-out

The water content C_w near the bulk surface is determined by the nature of the membrane and the osmotic pressure of the solution, i.e., by the thermodynamic potential μ_w. The water content C_w at any point x is determined by the local value of μ_w. Thus, with Eq. (14) and the correlation between current and water flow, i.e., Eq. (4), the state of the system is fully determined by the applied current. At a given current, with higher local friction coefficient μ_w decreases more steeply and C_w decreases in a self-reinforcing effect. The relation between the driving force X_w and the applied current is given by

$$C_w X_w = -\frac{I}{2F}\left[f_{wm} + f_{w+}\left(\frac{2C_w}{C_+} + 1 \right) \right] = -\frac{I\Phi}{2F} \tag{15}$$

Integrating from $x = 0$ at the membrane surface adjacent to the bulk to Δx at the bipolar interface

$$\int_{\mu_w^0}^{\mu_w^i} \frac{C_w}{\Phi} d\mu_w = \frac{I\Delta x}{2F} \tag{16}$$

The decisive parameter for dry-out is the water content at the interface. In a membrane layer with very small water content, the friction coefficients are expected to increase drastically, allowing very little water flow. Though no information in these specific conditions is available it is reasonable to assume that the friction coefficients depend on the water content rather than on the thermodynamic potential, i.e., on C_w and not directly on $d\mu_w$.
Expressing the thermodynamic potential and the osmotic pressure by the vapor pressure of the

water, p

$$d\mu_w = RT d\ln p \tag{17}$$

$$C_w \frac{d\mu_w}{dC_w} = RT \frac{d\ln p}{d\ln C_w} \tag{18}$$

$$\frac{d\ln p}{d\ln C_w} = W \tag{19}$$

The thermodynamic parameter W is an independently measurable property of the membrane material. The water content of solutions with the same water vapor pressure may vary substantially with the nature of the solution. There are some well-characterized inorganic solutions and polyelectrolyte solutions that are used for drying air due to their low vapor pressure.

$$\int_{C_w^0}^{C_w^i} \frac{W}{\Phi} dC_w = \frac{I\Delta x}{2FRT} \tag{20}$$

Eq. (20) states that the water content of the membrane near the interface is determined by the applied current and by the membrane properties. For higher values of W, the interval $C_w^0 - C_w^i$ will be smaller. With lower friction coefficients for higher C_w^i, these are mutually reinforcing dependencies.

7. Conclusions

It was shown previously that introducing a polymer of higher charge density into the interface enhances water splitting (Balster 2006). The present analysis leads to a quantitative criterion for the choice of polymers, which may mitigate the dry-out at high current densities. It is well known that membrane permeability to a solute depends on a distribution coefficient and a diffusion coefficient - on thermodynamic and kinetic interactions between solute and membrane. Further, the interaction between salt and water flow and with different solutes may contribute to the process. In BPMs there is in addition a different, unique, correlation between the two major flows, current and water flow. For highly selective BPMs, one driving force, the externally applied potential, determines all. The membrane properties necessary for effective BPM function are different from those essential in other electromembrane processes, and internally contradictory. For ED and Donnan Dialysis, high permselectivity and low water flow by osmosis and electro-osmosis are required. In BPM high permselectivity is essential too, but water supply to the interface should not be hampered by too low water permeability and this may interfere with the choice of the best material to achieve permselectivity.

It is shown here that for adequate water flow not the uptake in contact with the bulk solutions but the dependence of water content on osmotic pressure is critical. A water-retaining parameter W is defined

$$W = \frac{d\ln p}{d\ln C_w}$$

High *W*, probably found in highly charged as well as hydrophilic polymers, would not lead to highly selective CEM and AEM as components for BPM. However, a polymer chosen for its high *W,* introduced in a layer near the interface, may suffice to suppress somewhat the steep decrease of water content there. This will increase the current density at which water flow is blocked.

A composite CEM consisting of highly selective material and a thin layer characterized by high *W* might help to fulfill the contradicting requirements for an effective BPM.

Acknowledgements

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ED

List of symbols

C	concentration	[mol m^{-3}]
F	Faraday constant	[A s eq^{-1}]
f	friction density	[J s mol^{-1} m^{-2}]
I	current density	[A m^{-2}]
J	molar flow	[mol m^{-2} m^{-1}]
J_y	volume flow	[m s^{-1}]
L	transport coefficient	[mol^2 N^{-1} m^{-2} s^1]
L_p	hydraulic permeability	[m^3 N^{-1} s^{-1}]
p	pressure	[Pa]
p_0	partial vapor pressure of a solution	[Pa]
p_s	partial vapor pressure of a solution	[Pa]
R	gas constant	[J mol^{-1} K^{-1}]
T	temperature	[K]
V	partial molar volume	[m^3 mol^{-1}]
v	component average velocity	[m s^{-1}]
X	driving force	[N mol^{-1}]
Δx	membrane thickness	[m]

Subscripts

$+$	referring to proton
0	referring to bulk solution
i	referring to interface
i, j	general component
m	referring to membrane polymer
w	referring to water

Superscripts

i	referring to interface
0	referring to bulk solution

Greek letters

β	Electro-osmotic coefficient	[-]
μ	chemical potential	[J mol^{-1}]
π	osmotic pressure	[Pa]