Modeling of Forward and Reverse Bias Conditions in Bipolar Membranes

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We present a set of analytical solutions to the problem of ion transport and field enhanced water dissociation in bipolar membranes. Most of the simplifying assumptions introduced in previous models have now been removed. Particular attention is paid to the effects caused by a non-abrupt, smooth junction at the cation layer/anion layer interface, the forward bias characteristics of the current-voltage curve, and the membrane electrical resistance. Despite of the coupling between ion transport and the chemical reaction responsible of the field enhanced water dissociation, the solutions derived are simple, and can readily find application in multidisciplinary fields like the biophysical modeling of biological membranes and the separation processes involving synthetic bipolar ion exchange membranes.

I. Introduction

There have been proposed a number of theoretical models to describe ion transport and field enhanced water dissociation in bipolar membranes [1-7]. Though these models describe some of the features experimentally observed, a theory accounting for the complete description of the transport phenomena is lacking. In particular, the following simplifying assumptions can be found in the literature: i) only two ions (either the water ions arising from the field enhanced water dissociation [2–4] or those coming from the fully dissociated electrolyte [8, 9]) are introduced; ii) the current-voltage *(I- V)* curve is studied either under forward or under reverse bias conditions [2–5] iii) an abrupt junction between the cationic layer (with negative fixed changes) and the anionic layer (with positive fixed charges) forming the bipolar membrane is

assumed [1, 5 – 11]; iv) the total externally applied voltage appears as a potential drop across the junction (i.e., the bulk membrane potential drops are ignored) [1, 4, 6, 7]; v) symmetry conditions for both the membrane layers and the bulk electrolyte solutions are introduced (in particular, the two bulk solution concentrations are assumed to be the same) [1, 5 – 7]; and vi) the case of zero or very small electric current is sometimes invoked [8, 12].

We have recently proposed [6,7] a simple theory allowing for both ion transport and field enhanced water dissociation (usually referred to as "water splitting" in the membrane literature [1, **3,** 7]) in bipolar membranes. The mechanism responsible for this dissociation was assumed to be a catalytic proton transfer reaction between the fixed groups and the water at the bipolar junction [2– 5]. The model was based on the application of some of the concepts used in the solid state p-n junction theory to bipolar membranes [1, 13] and did not involve the simplifying assumptions i) and vi). Also, assumptions ii) and v) were partially removed. Despite the complex phenomena which result from the coupling of ion transport and chemical reactions, a rather

simple approach explained reasonably well the experimental trends observed in the *I-V* curves: high conductivity under forward bias conditions and high impedance first, and then field enhanced water dissociation for high enough applied voltages under reverse bias conditions. Comparison between theory and experiments [7, 14] provided reasonable values for the parameters introduced in the model. Also, the temperature effects on the *I-* V curves were satisfactorily accounted for [7, 14]. However, other effects not explicitly included in the model (see points ii)-v) above) can also play an important role in the bipolar membrane characterization.

We present now a more complete theory accounting for the above mentioned effects. Special attention is paid to the case of a non-abrupt junction as well as to the forward biased membrane. The first question is important because the performance of bipolar membranes largely depends on the structure of the space charge region which appears at the bipolar junction under reverse bias conditions (note that this current efficiency depends on the water dissociation phenomena occurring at this junction [1, 5 – 7]). The study of the forward biased membrane is of interest because it can permit an accurate determination of the transport parameters which also appear in the modelling of the reverse biased membrane. Once these parameters have been determined, we can concentrate on the characteristics of the water dissociation phenomena occurring in the reverse biased membrane. In particular, determination of the fixed charge densities, the diffusion coefficients, etc. under forward bias conditions will allow for an unambiguous characterization of the water dissociation reaction. In this sense, our results can be of interest in the multidisciplinary fields where the "bipolar membrane" model finds application [2, 5, 11, 12, 14 – 16].

II Theoretical Model

Fig. 1 shows a bipolar membrane separating two solutions of the same univalent electrolyte (The extension to other binary electrolyte systems is straightforward). The cationic layer extends from $x = -d_L$ to $x = 0$ and contains
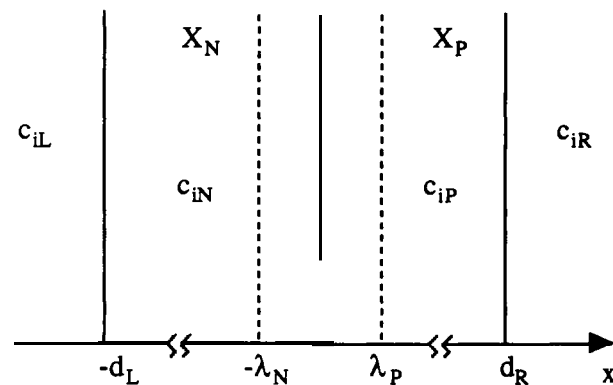

Fig. 1
Sketch of the bipolar membrane. The space charge region lies between $x = -\lambda_N$ and $x = \lambda_P$. c_{iN} and c_{iP} denote the concentrations of the ith species in the cation and the anion exchange layers, respectively

a concentration X_N of negatively charged fixed groups; the anion exchange layer lies between $x = 0$ and $x = d_R$ and has a concentration X_P of positively charged fixed groups. These concentrations are supposed to be uniform (at least) in the bulk of the membranes. c_i stands for the concentration of the i-th species (i = 1 for salt cations, i = 2 for salt anions, i = 3 for hydrogen ions and i = 4 for hydroxyl ions), subscripts L, R, N and P refer to the left and right bulk aqueous solutions, and to the cationic and anionic layers of the bipolar membrane, respectively. The system is assumed to be isothermal and at steady state. Solvent flow is neglected.

The Donnan equilibrium relationships [1] for the two membrane solution interfaces are

$$\frac{c_{1N}(-d_L)}{c_{1L}} = \frac{c_{2L}}{c_{2N}(-d_L)} = \frac{c_{3N}(-d_L)}{c_{3L}} = \frac{c_{4L}}{c_{4N}(-d_L)} \ , \quad (1a)$$

$$\frac{c_{1P}(d_R)}{c_{1R}} = \frac{c_{2R}}{c_{2P}(d_R)} = \frac{c_{3P}(d_R)}{c_{3R}} = \frac{c_{4R}}{c_{4P}(d_R)} \ . \quad (1b)$$

The ion exchange layer thicknesses d_L and d_R are assumed to be very thick compared with the typical Debye lengths of the system. Therefore, the local electroneutrality condition holds in every bulk phase

$$c_{1K} + c_{3K} = c_{2K} + c_{4K} \ , \quad K = L, R, \quad (2a)$$

$$c_{1N} + c_{3N} = c_{2N} + c_{4N} + X_N \ , \quad -d_L \leq x \leq -\lambda_N \ , \quad (2b)$$

$$c_{1P} + c_{3P} + X_P = c_{2P} + c_{4P} \ , \quad \lambda_P \leq x \leq d_R \ . \quad (2c)$$

From Eqs. (1) and (2), the following interfacial concentrations result

$$c_{iN}(-d_L) = \frac{c_{iL}}{c_{1L} + c_{3L}} \cdot [\sqrt{X_N^2/4 + (c_{1L} + c_{3L})^2} + (-1)^{i+1} X_N/2] \ , \quad (3a)$$

$$c_{iP}(-d_R) = \frac{c_{iR}}{c_{1R} + c_{3R}} \cdot [\sqrt{X_P^2/4 + (c_{1R} + c_{3R})^2} + (-1)^i X_P/2] \ , \quad (3b)$$

for $i = 1, 2, 3, 4$, and the Donnan potential differences can be expressed as

$$\Delta \Psi_{D,L} = \ln \frac{c_{1N}(-d_L)}{c_{1L}} \ , \quad (4a)$$

$$\Delta \Psi_{D,R} = \ln \frac{c_{1R}}{c_{1P}(d_R)} \ , \quad (4b)$$

where $\Psi = F\phi/RT$ denotes the dimensionless electric potential, and F, R, T have their usual meaning [6]. Δ refers to left minus right values.

The ion fluxes J_{iK} through the ion exchange layers are described by the Nernst-Planck equations:

$$J_{iK} = -D_{iK} \left[\frac{dc_{iK}}{dx} + (-1)^{i+1} c_{iK} \frac{d\Psi}{dx} \right] ,$$
$$i = 1,2,3,4, \; ; \; K = N,P , \tag{5}$$

where D_{iK} is the diffusion coefficient of i-th species in region K. The fluxes in Eq. (5) must satisfy the continuity equations

$$\frac{dJ_{iK}}{dx} = 0 , \quad i = 1,2 ; \quad K = N,P \tag{6a}$$

for the salt ions, and

$$\frac{dJ_{iK}}{dx} = g - r , \quad i = 3,4 ; \quad K = N,P \tag{6b}$$

for the water ions, where g and r are respectively the generation and recombination rates of the ions coming from the water dissociation reaction. The high electric fields enhancing the water dissociation mainly occur in the thin space charge layer formed at the bipolar junction under reverse bias conditions [1, 4, 6, 7, 14]. Therefore, we should expect that under forward bias conditions g = r throughout the membrane. However, under reverse bias conditions we have that $g \gg r$ over the space charge region, since due to the small thickness of this region ($-10 - 10^2$ Å) the geometry for recombination is very poor while the generation is appreciably increased by the high electric fields present there [1, 3, 4, 6, 7, 14]. This generation rate can be written as

$$g = k_d n = k_d^0 n \exp(\alpha FE/RT) , \tag{7}$$

where n is the concentration of active sites in the membrane where the field enhanced water dissociation occurs. According to previous theoretical and experimental analyses [1, 4, 5, 7, 14], we have taken an exponential electric field dependence for the forward rate constant of the water dissociation reaction. In Eq. (13) a is a characteristic length for the dissociation reaction ($a - 10^{-10}$ m [1, 4, 5, 7, 14]), E is a typical value for the electric field in the space charge region ($E - 10^8 - 10^9$ V/m), and k_d^0 can be written as

$$k_d^0 = A \exp(-E_a/RT) . \tag{8}$$

In Eq. (8), A is the frequency factor or pre-exponential factor and E_a is the activation energy of the process ($E_a \sim 10 - 10^2$ kJ/mol [5, 7, 141]).

Finally, the total electric current passing through the membrane is

$$I = F(J_{1K} - J_{2K} + J_{3K} - J_{4K}) , \quad K = N,P . \tag{9}$$

It is worth noting that J_{1K} and J_{2K} are constant throughout the membrane (see Eq. (6a)). Also, J_{3K} and J_{4K} will be practically constant in the bulk of the two membrane layers, where g = r. Under reverse bias conditions, $J_{3K} \neq J_{4K}$, but $J_{3K} - J_{4K}$ is constant throughout the membrane (see Eq. (6b)).

Note that the present model assumes that the hydrodynamic permeability of the membrane is high enough so that the water molecules consumed in the dissociation reaction are compensated for by the water arriving at the junction from the bulk phases. This is a reasonable approximation except for extremely high currents, when the junction drying can be a major problem [17].

Let us consider separately the cases of the forward and reverse biased membrane.

1. Forward Biased Membrane

This case corresponds to positive values of the total potential drop. For such values the water dissociation effects are negligible and the only ions contributing to the electric current are the salt ions. Therefore, we will consider only the salt ions in the study of the forward biased membrane.

The Nernst-Planck equations (5) can also be expressed as

$$j_{1K} + j_{2K} = -\frac{du_K}{dx} \mp X_K \frac{d\Psi}{dx} , \quad K = N,P , \tag{10}$$

$$j_{1K} - j_{2K} = -u_K \frac{d\Psi}{dx} , \quad K = N,P , \tag{11}$$

where

$$j_{iK} \equiv J_{iK}/D_{iK} , \quad i = 1,2 ; \quad K = N,P , \tag{12}$$

and

$$u_K \equiv c_{1K} + c_{2K} , \quad K = N,P . \tag{13}$$

The minus sign in Eq. (10) corresponds to K = N, and the plus sign to K = P.

Eq. (9) for the total electric current now becomes

$$I = F \frac{\gamma D_K}{1 + \gamma \tau_K} (j_{1K} + j_{2K}) , \quad K = N,P , \tag{14}$$

where

$$D_K \equiv \frac{2 D_{1K} D_{2K}}{D_{1K} + D_{2K}} , \quad K = N,P , \tag{15}$$

is the salt diffusion coefficient in region K,

$$\tau_K \equiv \frac{D_{2K} - D_{1K}}{D_{1K} + D_{2K}} , \quad K = N,P , \tag{16}$$

is a parameter related to the asymmetry in the ionic diffusion coefficients, and

$$\gamma \equiv \frac{J_{1K} - J_{2K}}{J_{1K} + J_{2K}} \ , \quad K = N, P \ . \tag{17}$$

Integration of Eqs. (10) yields

$$-d_L(j_{1N} + j_{2N}) = u_N(-\lambda_N) - u_N(-d_L) - X_N \Delta \Psi_N \ , \tag{18}$$

$$-d_R(j_{1P} + j_{2P}) = u_P(d_R) - u_P(\lambda_P) + X_P \Delta \Psi_P \ , \tag{19}$$

where $\lambda_{N,P}$ have been neglected when compared to $d_{L,R}$. Also, by using Eq. (11), the potential drops in the bulk of the two ion exchange layers are

$$\Delta \Psi_N = \Gamma_N \ln \frac{u_N(-d_L) - X_N \Gamma_N}{u_N(-\lambda_N) - X_N \Gamma_N} \ , \tag{20}$$

and

$$\Delta \Psi_P = \Gamma_P \ln \frac{u_P(\lambda_P) + X_P \Gamma_P}{u_P(d_R) + X_P \Gamma_P} \ , \tag{21}$$

where

$$\Gamma_K \equiv \frac{j_{1K} - j_{2K}}{j_{1K} + j_{2K}} = \frac{\gamma + \tau_K}{1 + \gamma \tau_K} \ , \quad K = N, P \ . \tag{22}$$

Finally, the Donnan equilibrium at the bipolar junction leads to

$$4 c_{1N}(-\lambda_N) c_{2N}(-\lambda_N) = u_N^2(-\lambda_N) - X_N^2 = u_P^2(\lambda_P) - X_P^2$$
$$= 4 c_{1P}(\lambda_P) c_{2P}(\lambda_P) \ . \tag{23}$$

The Donnan potential at this junction is

$$\Delta \Psi_{D,J} = \ln \frac{c_{1P}(\lambda_P)}{c_{1N}(-\lambda_N)} = \ln \frac{u_P(\lambda_P) - X_P}{u_N(-\lambda_N) + X_N} \ . \tag{24}$$

Division of Eq. (18) by Eq. (19), and further substitution of $(j_{1K} + j_{2K})$ from Eq. (14), yields

$$\frac{d_L D_P(1 + \gamma \tau_N)}{d_R D_N(1 + \gamma \tau_P)} = \frac{u_N(-\lambda_N) - u_N(-d_L) - X_N \Delta \Psi_N}{u_P(d_R) - u_P(\lambda_P) + X_P \Delta \Psi_P} \ . \tag{25}$$

Eqs. (23) and (25) can be solved for $u_N(-\lambda_N)$ and $u_P(\lambda_P)$ once a value for γ is provided. (Note that $u_N(-d_L)$ and $u_P(d_R)$ are known from Eqs. (3)). Then, Eqs. (14) and (18) can be used to obtain the electric current I, and the total potential drop across the membrane is computed through addition of the individual drops as

$$\Delta \Psi_{D,L} + \Delta \Psi_N + \Delta \Psi_{D,J} + \Delta \Psi_P + \Delta \Psi_{D,R} \equiv F V / R T \ . \tag{26}$$

This procedure gives the general solution for the forward biased membrane. The current-voltage curve is obtained in parametric form, with V and **I** expressed as functions of y.

However, Eqs. (20) and (21) can not be applied to those cases where $\Gamma_K = 0$. In particular, the symmetrical case:

$$c_{iK} \equiv c_0 \ , \quad i = 1, 2 \ , \quad K = L, R \ , \tag{27}$$

$$D_{iK} \equiv D \ , \quad i = 1, 2 \ ; \quad K = N, P \ , \tag{28}$$

$$d_K \equiv d \ , \quad K = N, P \ , \tag{29}$$

$$X_K \equiv X \ , \quad K = N, P \ , \tag{30}$$

calls for an alternative solution to Eqs. (10) and (11). This solution turns out to be very simple since for this case

$$j_{1K} = -j_{2K} = I/2FD \ , \quad K = N, P \ . \tag{31}$$

The **I** − V curve now obtained is

$$FV/RT = \ln \frac{\sqrt{X^2 + 4c_0^2} + X}{\sqrt{X^2 + 4c_0^2} - X}$$
$$+ \frac{2}{X} [\sqrt{X^2 + 4c_0^2 + 2XdI/DF} - \sqrt{X^2 + 4c_0^2}]$$
$$+ \ln \frac{\sqrt{X^2 + 4c_0^2 + 2XdI/DF} - X}{\sqrt{X^2 + 4c_0^2 + 2XdI/DF} + X} \ . \tag{32}$$

Then, V shows a linear dependence with **I** in the low current limit $(I \ll FDX/2d)$

$$FV/RT \simeq Id \frac{\sqrt{X^2 + 4c_0^2}}{2FDc_0^2} \ , \tag{33}$$

and a power dependence in the high current limit $(I \gg FDX/2d)$

$$FV/RT \simeq 2\sqrt{2Id/DFX} \ . \tag{34}$$

2. Reverse Biased Membrane with Abrupt Junction

The full system of Eqs. (1) − (9) for the reverse biased membrane can be solved with the same procedure employed for the forward biased case. Unfortunately, the resulting expressions are very involved. We decided then to present a simplified model that gives reasonable results for our problem. In particular we will introduce the following simplifications:

I) The fixed charge concentrations are much greater than the bulk electrolyte concentrations. The salt coion concentration is very small, and decreases towards the bipolar junction. On the other hand, the electric field in the bulk of the ion exchange layers is not very strong. Therefore, the migration term for the salt coion in each one of these layers is very small. This assumption is widely used in solid state physics [13].

II) It can be easily proved that the flux and concentration for the minority water ion (i.e., hydrogen or hydroxyl ion) in each one of the two ion exchange layers are very small.

III) The flux for the majority water ion is nearly constant in the bulk of the ion-exchange layers since the electric field is not very high in these regions. Due to the relatively low values of the electric field, it can be assumed that the dissociation and the recombination rates are very similar there. Therefore, the majority water ion concentration is small, and we have neglected the migration term in the flux equation for the majority water ion in each ion exchange layer.

Assumptions I)–III) lead to the following transport equations in the cationic layer:

$$j_{1N} = -\frac{dc_{1N}}{dx} - c_{1N}\frac{d\Psi}{dx} , \qquad (35)$$

$$j_{2N} \simeq -\frac{dc_{2N}}{dx} , \qquad (36)$$

$$j_{3N} \simeq -\frac{dc_{3N}}{dx} , \qquad (37)$$

$$j_{4N} \simeq 0 . \qquad (38)$$

An analogous set of equations can be written for the anionic layer. The above equations are easily integrated to give

$$c_{1N}(-\lambda_N) = c_{1N}(-d_L) - (j_{2N} - j_{3N})d_L , \qquad (39)$$

$$c_{2N}(-\lambda_N) = c_{2N}(-d_L) - j_{2N}d_L , \qquad (40)$$

$$c_{1P}(\lambda_P) = c_{1P}(d_R) + j_{1P}d_R , \qquad (41)$$

$$c_{2P}(\lambda_P) = c_{2P}(d_R) + (j_{1P} - j_{4P})d_R , \qquad (42)$$

and

$$\Delta\Psi_N = \frac{j_{1N} + j_{3N} - j_{2N}}{j_{3N} - j_{2N}} \ln\left[1 + \frac{(j_{3N} - j_{2N})d_L}{c_{1N}(-d_L)}\right] , \qquad (43)$$

$$\Delta\Psi_P = \frac{j_{1P} - j_{2P} - j_{4P}}{j_{1P} - j_{4P}} \ln\left[1 + \frac{(j_{1P} - j_{4P})d_R}{c_{2P}(d_R)}\right] . \qquad (44)$$

In order to determine the flux j_{3N}, Eq. (6b) for $i = 3$ must be integrated from $x = -\lambda_N$ to $x = \lambda_P$. Then,

$$D_{3P}j_{3P} - D_{3N}j_{3N} \simeq -D_{3N}j_{3N} \simeq \int_{-\lambda_N}^{\lambda_P} k_d n\,dx$$
$$= k_d^0 n\lambda \exp(\alpha FE(0)/RT) , \qquad (45)$$

where

$$\lambda \equiv \lambda_N + \lambda_P \qquad (46)$$

is the thickness of the space charge region, and E(0) the maximum value attained by the electric field through the space charge region. Substituting $E(x) \simeq E(0)$ in Eq. (45) allows for an immediate integration, but overestimates the water dissociation effects. However, more exact computations as well as the results in Refs. 4 and 14 show that proceeding in this way does not change the order of magnitude of the water dissociation reaction parameters obtained from the comparison of theory and experiment. Given the uncertainties associated to other membrane parameters, the above approximation can be considered as reasonable.

According to the depleted layer model for the abrupt junction [1, 4, 6, 11, 13] (see Fig. 1), the electric field at x = 0 is given by

$$E(0) = \left[\frac{2F}{\varepsilon_r\varepsilon_0}(-\Delta\Psi_{D,J})\frac{X_N X_P}{X_N + X_P}\right]^{1/2} , \qquad (47)$$

and the thickness of the space charge region is

$$\lambda = \left[\frac{2\varepsilon_r\varepsilon_0}{F}(-\Delta\Psi_{D,J})\frac{X_N + X_P}{X_N X_P}\right]^{1/2} , \qquad (48)$$

where ε_r is the dielectric constant of the bipolar junction and ε_0 the permittivity of free space. Note that the depleted layer model assumes that no mobile ions exist within the space charge region, being the total charge density of Poisson's equation equal to the fixed charge concentration in the membrane [6, 13]. This is certainly the case for the reverse biased membrane.

The dependence of j_{3N} on the Donnan potential at the bipolar interface suggests to look for a solution of the transport equations parametric in $\Delta\Psi_{D,J}$. Once j_{3N} is known, we can make use of Eq. (6b) to obtain j_{4P} as

$$j_{4P} = -\frac{D_{3N}}{D_{4P}}j_{3N} . \qquad (49)$$

We can also make use of Eq. (6a) to obtain the relationships

$$j_{iP} = \frac{D_{iN}}{D_{iP}}j_{iN} , \quad i = 1,2 \qquad (50)$$

Then, we only have two undetermined fluxes, say j_{1N} and j_{2N}, which can be determined by using the Donnan equilibrium conditions at the bipolar junction:

$$c_{1P}(\lambda_P) = c_{1N}(-\lambda_N)\theta , \qquad (51a)$$

$$c_{2N}(-\lambda_N) = c_{2P}(\lambda_P)\theta , \quad \theta \equiv \exp(\Delta\Psi_{D,J}) , \qquad (51b)$$

with the result

$$j_{1N} = \frac{D_{1P}}{D_{1N}}\frac{1}{d_R(1-\theta^2)}\left\{-c_{1P}(d_R)\right.$$
$$+ [c_{1N}(-d_L) - c_{2N}(-d_L) + j_{3N}d_L]\theta$$
$$+ \left.\left[c_{2P}(d_R) + \frac{D_{3N}}{D_{4P}}d_R j_{3N}\right]\theta^2\right\} , \qquad (52a)$$

$$j_{2N} = \frac{1}{d_L(\theta^2 - 1)} \left\{ -c_{2N}(-d_L) \right.$$

$$+ \left[c_{2P}(d_R) - c_{1P}(d_R) + \frac{D_{3N}}{D_{4P}} j_{3N} d_R \right] \theta$$

$$\left. + [c_{1N}(-d_L) + d_L j_{3N}] \theta^2 \right\} \ . \tag{52b}$$

We have obtained now the dependences $I(\Delta \Psi_{D,J})$ (see Eq. (9)), and $V(\Delta \Psi_{D,J})$ (see Eq. (26)). Therefore, the complete $I - V$ curve can be computed in parameteric form.

3. Reverse Biased Membrane with Smooth Junction

Let us now discuss in more detail the nature of the bipolar junction at $x = 0$. As stated above, the picture usually invoked for this interface is based on the depleted layer model for the abrupt junction. However, taking into account the preparation procedures of the bipolar membranes [2, 14, 15, 18 – 20], the non-abrupt junction model can be more realistic for many cases of interest. Then we have tried to put the junction model one step further. Although it is possible to solve this problem for a general membrane charge distribution, we are considering a simple case where the membrane charge density varies linearly with position over a region wider than the space charge region. Figure 2 shows the membrane charge density profiles. Now, according to the depleted layer model for the non-abrupt junction, the charge density in the space charge region is

$$\rho(x) = F[X_P(x) - X_N(x)] = F[(X_0 + \delta_P x) - (X_0 - \delta_N x)]$$
$$= F(\delta_P + \delta_N)x \ , \tag{53}$$

where $X_0 \equiv X_K(0)$, and δ_K are the absolute values of the slopes of the fixed charge concentrations $X_K(x)$. The latter are assumed to depend linearly on the position x over a region wider than the space charge layer, which is very reasonable. The solution of the Poisson equation under boundary conditions
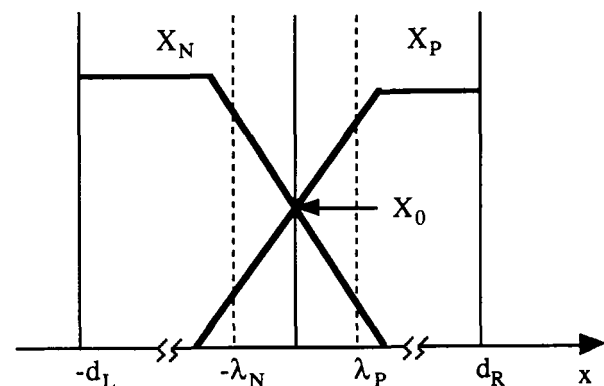

Fig. 2
Schematic view of a bipolar membrane with a non-abrupt junction. X_0 is the value attained at $x = 0$ by the fixed charge concentration in the cation and anion exchange layers

$$\left(\frac{d\Psi}{dx} \right)_{x = -\lambda_N} = \left(\frac{d\Psi}{dx} \right)_{x = \lambda_P} \ , \tag{54a}$$

$$\Psi(0) = 0 \ , \tag{54b}$$

gives

$$E(0) \simeq \left[\frac{F}{\varepsilon_r \varepsilon_0} \frac{\delta_N + \delta_P}{2} \left(\frac{3RT\Delta\Psi_{D,J}}{4F} \right)^2 \right]^{1/3} \ , \tag{55}$$

and

$$\lambda_N = \lambda_P = \left[\frac{3}{2} \frac{\varepsilon_r \varepsilon_0 RT}{F^2} \frac{(-\Delta\Psi_{D,J})}{\delta_N + \delta_P} \right]^{1/3} \ , \tag{56}$$

where we have neglected $(d\Psi/dx)_{-\lambda_N}$ against $(d\Psi/dx)_0$. Eqs. (55) and (56) replace Eqs. (47) and (48) above respectively, and now the transport equations can be solved as in the case of the abrupt junction.

Eqs. (35) – (38) lead to linear concentration profiles for the water ions and the salt coions. It is now worth to consider the limiting case where assumptions I – III) are no longer valid. This limit corresponds to very high electric currents. For simplicity, we will study only the symmetrical situation. For this case,

$$j_{iP} = j_{iN} \equiv j_i \ , \quad i = 1,2 \ , \tag{57}$$

$$j_{4P} = -j_{3N} \ . \tag{58}$$

At high enough voltages, we have that

$$j_{3N} \gg j_1, j_2 \ . \tag{59}$$

In addition, if we assume that the coions can be neglected in the bulk of the cationic layer, the electroneutrality condition gives

$$c_{1N} + c_{3N} \simeq X \ . \tag{60}$$

Introduction of Eqs. (57 – 60) permits a straightforward integration of the Nernst-Planck equations to give the profiles

$$\Psi(x) = \Psi(-d) - \frac{I}{FDX}(x+d) \ , \tag{61}$$

$$c_{1N}(x) = X \exp [I(x+d)/FDX] \ , \tag{62}$$

$$c_{3N}(x) = X\{1 - \exp [I(x+d)/FDX]\} \ . \tag{63}$$

For the anionic layer, symmetry considerations lead to

$$c_{2P}(x) = c_{1N}(-x) \ , \tag{64}$$

$$c_{4P}(x) = c_{3N}(-x) \ . \tag{65}$$

Note that $I - FDX/d \sim 10^2 - 10^3 \, A/m^2$ corresponds indeed to a very high electric current.

III Results and Discussion

The results obtained with the above model are presented in Figs. 3 – 7. Fig. 3 shows the **I** – V curve over the full voltage range for different values of the bulk solution concentration ratio c_L/c_R. This ratio has been varied while keeping constant $c_L + c_R = 10^{-1}$ M $\ll X_N = X_P = 1\ M$. In plotting the curves of Fig. 3, we have considered as input data for the membrane parameters of the model a set of values having the same order of magnitude of those found experimentally for membrane M14 in Ref. 14 ($k_d^0 n \sim 10^4$ mol/m^3 s, $a \sim 10$-'Om, $E_a \sim 35$ kJ/mol, $\varepsilon_r = 25$, $D_{iK} \sim 10^{-9}$ m^2/s ($i=$ 1,2,3,4, K = N,P), $d_L = d_R \sim 10^{-4}$ m). We see that current increases very rapidly with voltage for the forward biased membrane (Note that the voltage scale has been enlarged for this case in Fig. 3. Bearing in mind this fact, it becomes apparent that the shape of the **I** – V curve closely follows those experimentally found in the literature [5, 11, 14, 15, 18 – 20]). The influence of the concentration ratio is quite important for forward bias conditions. Indeed, if c_L/c_R 1, then a overvoltage due to the membrane potential appears, and this causes a shift respect to the externally applied potential drop [8]. This effect is negligible in the reverse bias case since much greater potential drops are now necessary for current to flow.

The two operation modes of the bipolar membrane are well-known [1, 2, 10, 18 -20]: for the forward biased membrane, the electric current leads to an accumulation of counterions at both sides of the bipolar junction between both layers. When this accumulation becomes very important, the Donnan exclusion is no longer operative and counterions can proceed to the other layer, where they are transported as coi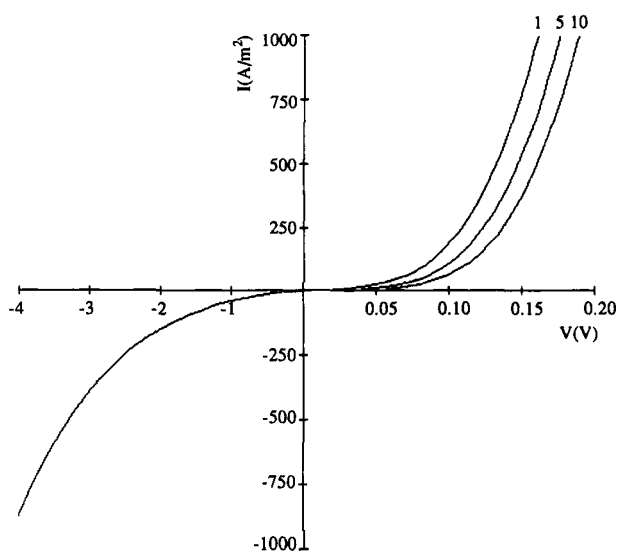ons. Therefore, high electric currents can flow under forward bias conditions when the applied voltage is high enough to overcome the Donnan exclusion effect. Consider now the case of reverse bias. For this case, the high electric field at the bipolar junction removes all the salt ions from there. A small limiting current is reached when the salt concentration at the junction becomes almost zero [1, 6, 10, 19], and then the onset of the field-enhanced water dissociation phenomenon allows for the passage of much higher currents [3 – 7, 21].

Fig. 4 gives the I – V curves obtained with four different models for the forward biased membrane. The case $c_L/c_R = 1$, $c_L + c_R = 10^{-1}$ M is analyzed. Curve 1 corresponds to the exact solution of the proposed model. Curve **2** has been obtained by neglecting the migration term in the flux equation for the coion, which leads immediately to linear concentration profiles for the coion concentration in each ion-exchange layer. The resulting I – V curve shows a reasonable agreement with the more exact curve 1 within the range of voltage values considered. Finally, curves 3 and 4 correspond to the exponential dependence found in Ref. 6 and to the linear dependence obtained in Ref. 9, respectively. Curve **3** overestimates the electric current for high voltages. Curve 4 is probably in error for small voltages, and results from the rather restrictive assumptions introduced in this reference. On the other hand, curves 1 – 3 clearly display that the Donnan exclusion effect holds up to a voltage of some 50 – 100 mV, which is indeed a typical value for the Donnan potential differences observed at the interfaces of highly charged membranes ($c_{L,R} \ll X_{N,P}$).

The effects of a non-abrupt junction at the two membrane layers of the reverse biased membrane have been considered in Fig. 5 (see Figs. 1 and 2 for details; note that the space charge region thickness depends on the properties of the transition region between the two bulk ion-exchange layers according to Eq. (56)). Again, we take $c_L + c_R =$
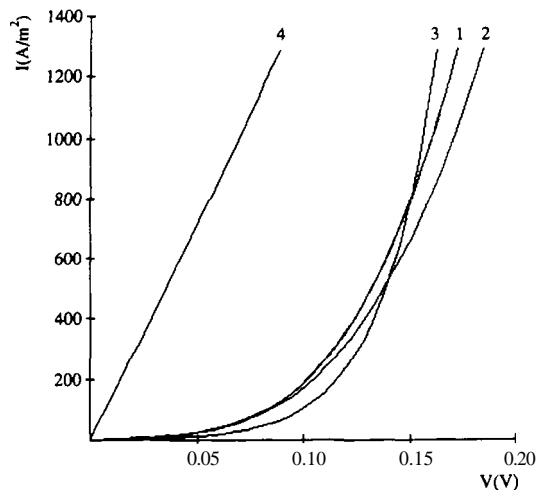

Fig. 3
I – V curve over the full voltage range for the bulk solution concentration ratios $c_L/c_R \simeq 1$, 5, and 10 with $c_L + c_R = 10^{-1}$ M. The membrane parameters employed in the model have the same order of magnitude of those found experimentally in Ref. 14 (see text). Note that the voltage scale has been enlarged for the case of the forward biased membrane

Fig. 4
I – V curves for the forward biased membrane obtained with four different models: (1) proposed model, (2) proposed model with the assumption of small electric current, (3) the model of Ref. 6, and (4) the model of Ref. 9. The case $c_L/c_R \simeq 1$ has been considered, and the membrane parameters are the same as in Fig. 3
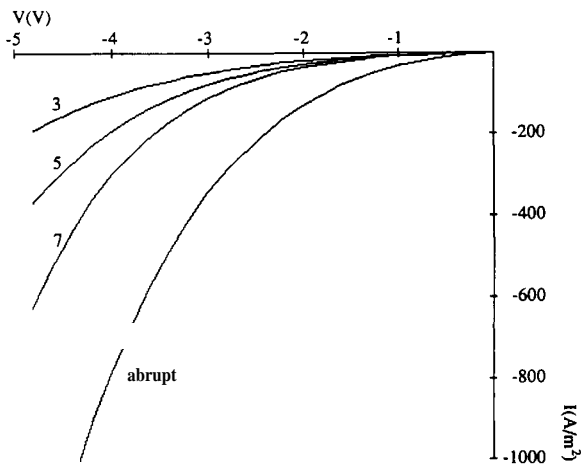
Fig. 5

I – V curves for the reverse biased membrane with a non-abrupt junction (see Fig. 2) at the interface between the two ion exchange layers. The curves are parametric in $q \equiv \delta/(X/d)$, $\delta_N = \delta_P \equiv \delta$, and correspond to $q = 3 \cdot 10^4$, $5 \cdot 10^4$, $7 \cdot 10^4$ and the abrupt junction (Fig. 1), respectively

Fig. 6

Membrane electrical resistance (defined as R = V/I) over the full voltage range for the same membrane parameters considered in Fig. 3 with $c_L/c_R = 10$. The voltage scale has been enlarged in the forward biased membrane case. The dashed line indicates the asymptotic behavior of R (see explanation in the text)

$10^{-1}\,\mathrm{M} \ll X_N = X_P = 1\,\mathrm{M}$. The curves in Fig. 5 are parametric in $q \equiv \delta/(X/d)$ (the labels in the figure correspond to the dimensionless numbers q = $3 \cdot 10^4$, $5 \cdot 10^4$, $7 \cdot 10^4$ and the abrupt junction, respectively). As expected, the abrupt junction presents the greater electric fields and, therefore, is the most efficient "water splitter" over the voltage range considered, this efficiency decreases rapidly when the values of $\delta_{N,P}$ get lower. Indeed, a very small current is transported by the water ions when q – 10^4 which corresponds to the fixed charge concentration decreasing from the bulk value to zero over a region 10^2 Å thick in each ion-exchange layer. It has been confirmed experimentally [2, 12, 14, 19, 22] that the nature (thickness, composition, etc.) of the junction between the ion exchange layers influences dramatically the properties of the bipolar membrane. In particular, very low junction resistances have been reported for thick transition regions [12]. Bearing in mind that the field enhanced water dissociation phenomenon occurs mainly at the bipolar junction, the formulation of models beyond the classical abrupt junction model is deemed to be necessary. This can be done now for each specific case within the scope of the model considered here.

The membrane electrical resistance (defined as R = V/I) is plotted in Fig. 6 over the full voltage range. Again, the membrane parameters employed are those experimentally found for membrane M 14 in Ref. 14. We have considered $c_L/c_R = 10$ with $c_L + c_R = 10^{-1}\,\mathrm{M}$ here. The resistance is much higher under reverse bias than under forward bias for usual voltages (-1 V). The rectification ratio obtained (-10^2) agrees with the order of magnitude of those observed experimentally [2, 19]. Note that the voltage scale has been enlarged for the forward biased membrane in Fig. 6 (if V– 1 V, then R – $10^{-4}\,\Omega\,\mathrm{m}^2$ according to our calculations). Let us consider first the reverse biased membrane. At small voltages, the rectification properties domain, and the resistance increases until a maximum value is
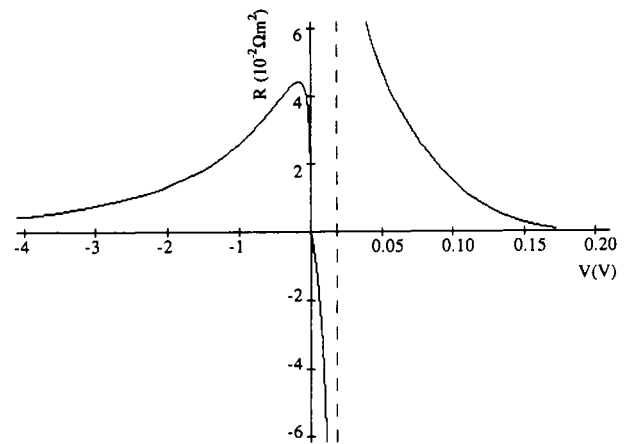
reached. This maximum gives the voltage from which the water dissociation effects are no longer negligible. For lower negative voltages the field enhanced water dissociation is very important, and the water ions appear as the dominant carriers. Accordingly, the resistance begins to drop. These facts have also been confirmed experimentally [14]. In the case of the forward biased membrane, we see that the Donnan exclusion effect holds (and the resistance is high) for small voltages. However, the resistance begins to drop to very low values when this exclusion fails, which occurs when the accumulation of ions at the membrane junction makes the salt concentration to be of the same order of magnitude as the fixed charge concentration (this requires a voltage of 50– 100 mV, as stated above). Note finally that R can attain very high (positive) and very low (negative) values in the vicinities of a critical voltage. This is a formal result that should be expected from the definition R = V/I. Indeed, since V is the externally applied potential drop and there is an additional potential difference due to the imposed concentration gradient (the so-called membrane potential), we have that very small negative (positive) values of **I** result when V is just slightly smaller (higher) than this membrane potential. This means that a negative, non-zero value for **I** should exist for the case V = 0, an effect that could not be seen in Fig. 3 due to the high values employed for the electric current scale (see Ref. 9 for a good account of this question).

Finally, Fig. 7 gives the concentration (in X units) profiles of counterions (ions 1 and 3 in the cationic layer, and 2 and 4 in the anionic layer) for a reverse biased membrane at high electric currents ($I = -2000\,\mathrm{A/m}^2$). Coion concentrations are omitted since they are very small. The profiles depart considerably from a linear behavior in this limiting case (see Eqs. (62)–(65)). For the salt ions the concentrations decrease from the membrane/solution interface to the bipolar junction. Conversely, the concentrations of the
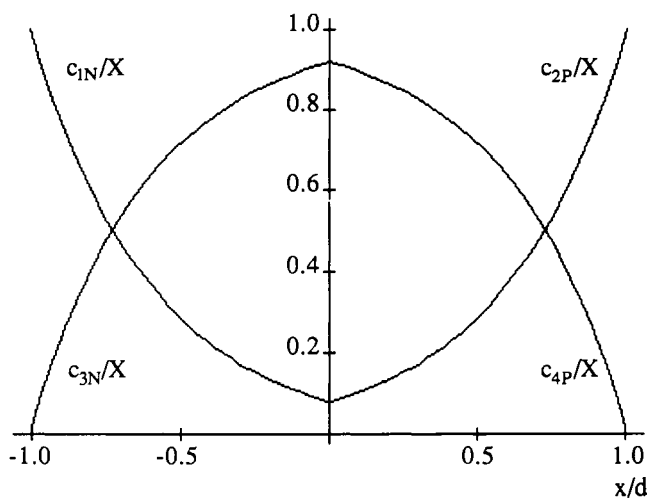
Fig. 7

Concentration profiles (scaled to the membrane fixed charge density $X_N = X_P \equiv X$) of counterions in each one of the two ion exchange layers for the reverse biased membrane at high electric current $(I = -2000 \, A/m^2)$. The space charge region has been omitted for the sake of clarity

water ion increase from the membrane/solution interface towards the junction. This should be expected since water dissociation effects are dominant at this junction for a reverse biased membrane at low enough negative voltages [23].

IV. Conclusions and Suggestions for Further Work

We have presented a physical model which can describe ion transport and water dissociation in bipolar membranes for a broad range of experimental conditions. The model is based on the Nernst-Planck equations as applied to membrane transport phenomena (see Refs. 24 – 25 for a complete account of the origin and limitations of these equations). Though a number of models have appeared in the literature, we must say that many of the simplifying assumptions previously invoked are not introduced here (see Introduction). Particular attention have been paid to three questions partially ignored in the literature: the effects of a non-abrupt junction, the forward bias characteristics of the current-voltage curve when a concentration gradient is imposed, and the membrane resistance behavior over the full voltage range. We have tried to relate our results to previous theoretical and experimental work in the field whenever possible.

Also, we would like to emphasize that despite the coupling between ion transport and the chemical reaction responsible for the field enhanced water dissociation, we have been able to derive a simple set of general, analytical solutions to the problem. Although the main emphasis of the paper is on the I- V curve, it is clear now that the interested reader can readily derive expressions for other experimental magnitudes (membrane potential, fluxes, etc.) from the results in section **II.** This question is thought to be of prime importance here, since the concept of "bipolar

membrane" is usually invoked in very different contexts which range from biophysical models for biological membranes [2, 11, 12] to technological applications involving synthetic membranes [5, 14– 16, 21, 22].

Finally, as suggestions for further work we would include: i) a thorough experimental study of the forward biased membrane characteristics (this was carried out for the reverse biased conditions in Ref. 14), and ii) the elaboration of specific models suited to the physicochemical nature of the junction and the particular water dissociation mechanism [3, 26 -28]. For instance, experimental data concerning a bipolar membrane with an intermediate neutral region have recently been reported [29]. Although some of the experimental trends there observed can be rationalized by using the theory presented in this paper (e.g., deviations from the abrupt junction result in a decrease of the water dissociation effects at a given voltage, as suggested by Fig. 5 for the particular junction structure here analysed), the elaboration of a model valid for these membranes would be necessary. Point ii) above is probably crucial in order to improve the efficiency of technologies based on bipolar membranes.

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