Effects of temperature and ion transport on water splitting in bipolar membranes*

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Abstract

We have considered the effects of temperature and ion transport on water splitting in bipolar membranes. The Nernst–Planck equations are employed for the ion fluxes, and the water splitting phenomenon is accounted for by means of either the Onsager theory of the Second Wien Effect or the Chemical Reaction model. Comparison between theory and experiment can be done on the basis of the experimental data by Zabolotskii et al. [Soviet Electrochem., 20 (1985) 1238]. Special attention is paid to the form of the current–voltage curves as well as to the variation of the current carried by the H⁺ and OH⁻ ions with the total electric current. It is found that the predictions derived from the Chemical Reaction model are generally in better agreement with experimental results than those obtained from the Second Wien Effect theory. Finally, we have applied the transport model to a fouled anion exchange membrane exhibiting a bipolar-like structure in order to study the influence of the fixed charge concentration in the fouling film on water splitting.

Keywords: bipolar membranes; ion-exchange membranes; water dissociation

1. Introduction

For different reasons bipolar membranes have recently received much attention: firstly, some biological membranes containing fixed charges exhibit rectification and capacitance properties that can be interpreted by means of a bipolar membrane model [1,2]; secondly, synthetic bipolar membranes have been extensively used for industrial purposes, e.g. the production of acids and bases from the corresponding salts [3]; in addition, some single-layered ion-exchange membranes used in electrodialysis may become a bipolar structure due to the deposition of a thin film of charged impurities on its surface [4–6]. When attempting to describe ion transport across bipolar membranes, at least four ionic species should be considered: the salt ions and the OH⁻ and H⁺ ions arising from water splitting. Some studies have dealt with the transport of only two ions (either the salt ions, or the water ions) across layered structures [7–10]. A complete description of ionic transport including all charged species has only been carried out under rather restrictive conditions.
Grossman [11] developed a model valid only for ordinary water dissociation, and numerically solved the corresponding equations. Basignana and Reiss [12] gave a simplified numerical treatment under symmetry conditions for nearly all the parameters involved (fixed charge concentration, diffusion coefficients, membrane thickness, etc.). In a previous paper [13], and following the ideas of Bassignana and Reiss, we have developed a simple model which includes multi-ionic transport, field-enhanced water dissociation, and space-charge effects on the basis of some of the concepts used in the solid state n-p junction.

In the above mentioned treatments, the central point is accounting for the massive presence of water ions detected through an increase in the pH of the surrounding solutions when electric current passes across the bipolar membrane [14,15]. This phenomenon is known as water splitting. Ordinary water dissociation cannot explain the magnitude of the observed electric current and the changes in pH [16]. It seems that a field-enhanced water dissociation should take place. It is generally believed that the hydrogen and hydroxyl ions originate in a very thin region at the interface between the two selective layers. The fact that pH changes are only observed under conditions of reverse bias suggests that the high electric field arising in that zone may promote the increase in the dissociation rate of water ions. Nevertheless, it is not exactly known which mechanism is responsible for this enhanced dissociation. In this context, different approaches have been made and the models proposed may be summarized as follows.

Simons and Khanarian [9] assume the existence of a neutral layer between the two selective layers. Field-enhanced water dissociation would take place in one or both of the interior surfaces of the charged regions where there is nonzero space charge density. The current–voltage (I–V) relation found is determined by the fact that all OH⁻ and H⁺ ions originated at these surfaces recombine in the neutral layer.

Other treatments [12,13,17] give an explanation of water splitting in terms of the Onsager’s theory of the Second Wien Effect (which gives an exponential dependence of the rate of dissociation with the electric field while the recombination rate remains unaffected), assuming that field-enhanced water dissociation takes place at the interface between the two selective layers.

Timashev and Karginova [10] propose a model in which the excess in OH⁻ and H⁺ ions would arise from chemical reactions between water and some fixed groups in the membrane matrix, as suggested previously by Simons [18]. These reactions would be accelerated by the presence of an intense electric field (≥10⁶ V/m) at the interface between the two charged layers.

The main objective of this work is to study the influence of the temperature on the ion transport across bipolar membranes and checking the validity of the above mentioned models for description of water splitting effects. Comparison between theory and experiment can be done on the basis of the experimental data by Zabolotskii et al. [19]. Special attention is paid to the form of I–V curves as well as to the electric current transported by the H⁺ and OH⁻ ions. In addition, the same transport model is applied to a fouled membrane, exhibiting a bipolar-like structure (it is assumed that water splitting takes place at the interface between the charged membrane and a film of impurities). The influence of the fixed charge concentration in the fouling film on the water splitting is also studied.

2. Models for ion transport and water splitting

Let us consider the isothermal, steady-state
ion transport in the bipolar membrane shown in Fig. 1. The cation-exchange layer contains a negative fixed charge concentration $X_N$, and extends from $x = -d_L$ to $x = 0$; the anion-exchange layer has a positive fixed charge concentration $X_P$ and lies between $x = 0$ and $x = d_R$. The ion concentrations are $c_i$ ($i=1$ stands for salt cations, $i=2$ for salt anions, $i=3$ for $H^+$ ions and $i=4$ for $OH^-$ ions). The fixed charge concentrations are assumed to be very large compared with the bulk concentrations of the four mobile ions. Subscripts L, R, N and P refer to the ion concentrations in the left and in the right bulk solutions and to the cation and anion exchange layers of the bipolar membrane respectively. Overbars denote inner membrane concentrations. For simplicity, neutral pH and equal salt ion concentrations are assumed in both bulk solutions surrounding the bipolar membrane, so that $c_{IL} = c_{IR} = c_0$ ($i=1,2$) and $c_{IL} = c_{IR} = c_b$ ($i=3,4$), where $c_0$ and $c_b$ denote the uni-univalent electrolyte and the water ion concentrations, respectively. Inner and outer ion concentrations are connected through the well known Donnan equilibrium conditions. The fluxes of the four ions across the bipolar membrane are described using the Nernst–Planck flux equations. Membrane thicknesses $d_L$ and $d_R$ are assumed to be very thick compared with the typical Debye length of the problem, so that the local electroneutrality condition holds in the bulk of both ion-exchange layers [20]. This electroneutrality condition fails in the space-charge zone extending from $x = -\lambda_N$ to $x = \lambda_P$. When a high reverse bias is applied to the system, this region becomes almost completely devoid of mobile ions. This situation is regarded to be analogous to that of the abrupt semiconductor n–p junction of solid-state physics [2,13]. Therefore, a Poisson equation must be considered in order to determine the value of the electric field over the thickness $\lambda$ of the space-charge region. In the abrupt junction approximation [2], the values of these magnitudes are:

$$E = \left[ \frac{2F}{\epsilon_r \epsilon_0} (-V) \frac{X_N X_P}{X_N + X_P} \right]^{1/2},$$

$$\lambda = \lambda_N + \lambda_P = \left[ \frac{2\epsilon_r \epsilon_0 (-V)}{F} \frac{X_N + X_P}{X_N X_P} \right]^{1/2},$$

where $F$ denotes the Faraday constant, $V$ the external bias applied and $\epsilon_r$ and $\epsilon_0$ the dielectric constant and the vacuum electric permittivity, respectively.

In the reverse bias regime, the electric resistance of the junction is very high compared with that of the bulk ion-exchange layers, and any external voltage applied to the system appears almost completely across the space-charge zone [12]. Water splitting effects are assumed to take place mainly in this junction because of the presence of large electric fields [16,18]. In the bulk of the ion-exchange layers, the generation and recombination rate constants for water ions take their equilibrium values $k^+_i$ and $k^-_i$ respectively.

Keeping in mind the above-mentioned assumptions, the concentration profiles of the four ions can be readily achieved [13]. From
these profiles, the resulting I–V curve takes the form:

\[ i = i_d \left[ \exp\left( \frac{FV}{RT} \right) - 1 \right] + i_i, \]

where

\[ i_i = F \left[ \frac{D_{1P} \tilde{c}_{1P}(d_R)}{d_R - \lambda_P} \tilde{c}_{1P}(d_R) + \frac{D_{2N} \tilde{c}_{2N}(-d_L)}{d_L - \lambda_N} \tilde{c}_{2N}(-d_L) + \frac{D_{3P} \beta_P \tilde{c}_{3P}(d_R) \cosh(\beta_P d_R)}{\sinh(\beta_P(d_R - \lambda_P))} + \frac{D_{4N} \beta_N \tilde{c}_{4N}(-d_L) \cosh(\beta_N d_L)}{\sinh(\beta_N(d_L - \lambda_N))} \right], \]

\[ \tilde{c}_{iN}(-d_i) = \frac{c_{iL}}{c_s + c_h} \left\{ (-1)^{i-1} \frac{X_N}{2} \right\} \]

\[ + \left[ \left( \frac{X_N}{2} \right)^2 + (c_s + c_h)^2 \right]^{1/2}, \quad i = 1, 2, 3, 4. \]

\[ \tilde{c}_{iP}(d_R) = \frac{c_{iR}}{c_s + c_h} \left\{ (-1)^{i-1} \frac{X_P}{2} \right\} \]

\[ + \left[ \left( \frac{X_P}{2} \right)^2 + (c_s + c_h)^2 \right]^{1/2}, \quad i = 1, 2, 3, 4. \]

In eqns. (4)–(8), \( D_{1N} \) and \( D_{1P} \) stand for the diffusion coefficients of the \( i \)-th ion in the cation- and anion-exchange layers respectively. In the following we will focus on synthetic bipolar membranes, whose typical thicknesses, of the order of \( 10^{-4} \) m, are much greater than that of the space charge zone \( (\lambda \sim 10^{-8} \) m) for the range of the external bias usually applied [13]; thus eqn. (4) becomes:

\[ i_i = F \left[ \frac{D_{1P} \tilde{c}_{1P}(d_R)}{d_R - \lambda_P} \tilde{c}_{1P}(d_R) + \frac{D_{2N} \tilde{c}_{2N}(-d_L)}{d_L - \lambda_N} \tilde{c}_{2N}(-d_L) + \frac{D_{3P} \beta_P \tilde{c}_{3P}(d_R) \coth(\beta_P d_R)}{\sinh(\beta_P(d_R - \lambda_P))} + \frac{D_{4N} \beta_N \tilde{c}_{4N}(-d_L) \coth(\beta_N d_L)}{\sinh(\beta_N(d_L - \lambda_N))} \right]. \]

Equation (3) is composed of two terms. The first one accounts for the electric current transported by the salt ions and the water ions generated under ordinary equilibrium dissociation, and shows the typical rectification experimentally observed in bipolar membranes [2,15]; therefore, the factor \( i_d \) can be interpreted as a limiting current. The second term accounts for the electric current carried out by the excess of water ions generated by the field-enhanced water splitting at the interface between the two layers of the bipolar membrane. It can be approximately evaluated upon integration of the water ion fluxes across the region extending from \( x = -\lambda_N \) to \( x = \lambda_P \), and yields:

\[ i_d = F(J_3 - J_4) \]

where \( J_i \) is the flux of the \( i \)-th ion (see ref. [13] for more details). As the high electric fields promote at the interface \( x=0 \) the water splitting, \( i_d \) is expected to vanish under forward bias conditions and to increase when a reverse bias is applied.

The actual mechanism causing the water
At high electric fields, dissociation prevails over recombination and the approximate integration of eqn. (10) yields:

$$i_d = -Fk_d c_w \lambda,$$  \hspace{1cm} (14)

where $c_w$ is the concentration of water at the interface.

Although the results of this model follow the observed experimental trends [13], some limitations should be pointed out. Onsager's theory has been successfully applied only up to $10^2$–$10^3$ V/m, and fields of the order of $10^5$–$10^6$ V/m may appear at the interface $x=0$. Hence, some effects not considered in this theory – e.g. rotation of water molecules – should be included [16]. On the other hand, Onsager's theory assumes the rate of recombination to be unaffected by the electric field. This should be valid for a homogeneous solution, but could be unrealistic for an interface under strong polarization. Finally, this model predicts identical behaviour for cation- and anion-exchange membranes. However, it has been extensively observed that water splitting occurs mainly in anion-exchange membranes [18,22,23].

**Chemical Reaction Model (CHR)**

The above mentioned effect of water splitting occurring mainly in anion-exchange membranes suggests the possibility that OH− and H+ ions may be produced in proton-transfer reactions between charged groups and water. However, according to experimental results, the forward rate constant $k_d$ of these reactions should be one or two orders of magnitude greater than that of equilibrium conditions $k_d^0$ [18]. The strong electric field at the interface may be the mechanism responsible for the increase in the rate constant, according to Ref. [10]:

$$k_d = k_d^0 \exp \left[ \frac{\alpha F}{RT} E \right],$$  \hspace{1cm} (15)

where $E$ is the electric field strength, $\alpha$ is the electron transfer coefficient, $R$ is the gas constant, and $T$ is the temperature.
where $\alpha$ is a characteristic parameter having the dimensions of length. Taking the typical values $X_N = X_P = 1 M$, $V = 1 V$, $\varepsilon_N = 20$, $\alpha = 10^{-10}$ m in eqn. (1), the electric field in the interface is $E \approx 10^8$ V/m, and eqn. (15) yields $k_d / k_3^a \approx 20$ for the enhancement of the forward rate constant of the chemical reaction. Note that the same value of the electric field would give $k_d / k_3^a \approx 10^6$ for the increase in the dissociation rate constant of water, according to Onsager's theory of the SWE (eqn. 13).

The current transported by OH$^-$ and H$^+$ ions is, by analogy to the eqn. (14),

$$i_d = -Fk_3n\lambda,$$

where $n$ denotes the concentration of active sites (number of groups/unit volume) where the reaction is taking place.

Neutral layer model

Simons and Khanarian [9] assume the existence of a neutral layer at the interface of the bipolar membrane in order to explain the large electric resistivity shown by the system under reverse bias conditions. According to these authors field-enhanced water dissociation would take place on one or both of the thin layers, inside the fixed charge regions, at their boundaries with the neutral layer. When a reverse bias is applied, the electric field in these layers is strong enough to promote a significant number of water ions available for conduction according to the SWE theory. Once the ions reach the neutral layer, they recombine themselves. Under steady state conditions accumulation and removal of OH$^-$ and H$^+$ ions in the neutral layer must be equilibrated. Due to the small value of the electric field in the neutral layer, the rate of dissociation of water would be much less than the rate of recombination in this zone. These assumptions lead to the following expression for the current carried by the water ions:

$$i_d = \frac{F(u_3 + u_4)^2}{k_3^0\delta^2} V^2,$$  \hspace{1cm} (17)

where $u_3$ and $u_4$ are the mobilities of the H$^+$ and OH$^-$ ions, and $\delta$ is the thickness of the neutral layer. Although eqn. (17) agrees with the experimental data in Ref. [9], it is not clear that all bipolar membranes showing water splitting properties exhibit a neutral layer between the two fixed charge regions. Moreover, water splitting seems more important in bipolar membranes made of a single matrix, where neutral layers are not likely to exist [3,15]. Since this model seems to be of interest only for certain membranes, we will not consider it here.

Effects of temperature

It has been experimentally recognised that water splitting effects are enhanced as temperature increases [19]. This enhancement of the electric current can be qualitatively explained if one assumes the following classical relationship for the rate constants involved in each model [24]:

$$k_3^0(T) = A \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (18)

where $A$ is the value of the rate constant at a reference temperature and $E_a$ is the activation energy of the process ($E_{aw}$ and $E_{aw}$ will refer to the chemical reaction and Second Wien Effect model respectively). Therefore, temperature effects can be taken into account by introducing this dependency in each one of the expressions for $i_d$ (see eqns. 13–16). In the following, $A$ and $E_a$ will be assumed constant. Both of them may depend also on temperature and nonlinear least square procedures would be required to fit the experimental data [24]. However, we shall deal here with this first approximation to the problem, that will prove to be good enough for our purposes.
3. Results

Some of the parameters involved in the equations given for the I–V relationship are not experimentally accessible and have to be estimated from other experimental data. For the CHR model these parameters are the following: \( n \) (active sites concentration), \( A \) (standard rate constant), \( \alpha \) (length dimension parameter), \( E_{\text{act}} \) (activation energy) and \( \varepsilon_r \) (relative permittivity in the membrane). For the SWE model, \( c_w \) (water concentration at the interface), \( E_{\text{sw}} \) and \( \varepsilon_r \). An estimation of their values has been made from experimental data reported by Zabolotskii et al. [19] for a commercial MB-1 bipolar membrane \( (X_N = X_p = 1 M) \):

\[
\begin{align*}
na & \approx 10^{13} \text{ mol-m}^{-2} \text{-sec}^{-1} \\
\alpha & \approx 5 \times 10^{-11} \text{ m} \\
E_{\text{act}} & \approx 51 \text{ kJ-mol}^{-1} \\
\varepsilon_r & \approx 26 \\
c_w & \approx 10^4 \text{ mol-m}^{-3} \\
E_{\text{sw}} & \approx 55 \text{ kJ-mol}^{-1}
\end{align*}
\]

(19)

All these values seem to be reasonable for a membrane with fixed charge of the order of 1 \( M \).

Fig. 2 shows the current–voltage curves for a synthetic bipolar membrane, under reverse bias conditions, computed for different temperatures. Typical values for fixed charge concentration, \( X_N = X_p = 1 M \), and thickness of the selective layers, \( d_i = d_0 = 10^{-4} \text{ m} \), have been used in the calculations. We have taken \( c_i = 10^{-2} M \) and \( c_i = 10^{-7} \text{ M} \). Also, \( D_{IN} = D_{IP} = 10^{-9} \text{ m}^2/\text{sec} \) \((i=1,2)\) and \( D_{IN} = D_{IP} = 10^{-8} \text{ m}^2/\text{sec} \) \((i=3,4)\). Figure 2(a) shows the results obtained under the assumption that the excess in \( \text{OH}^- \) and \( \text{H}^+ \) ions originates from the CHR model. In Fig. 2(b) the results obtained by assuming a SWE model can be seen. In both models, values for fitting parameters have been derived from the experimental results [19] which are also plotted. The two models give approximately the same order of magnitude for the electric current. Also, the trends for the increase of water splitting with temperature are similar, although the SWE model seems less sensitive to changes in temperature than the CHR model, at least within the range of fitting parameters chosen. For low voltages, the water splitting effects predicted by the CHR model are higher than those of the SWE model. It can be seen
that the agreement between the calculated curves and the experimental data is clearly better for the CHR model.

The quotient between the current $i_d$ carried by the water ions and the total current against the applied voltage is shown in Fig. 3, for the bipolar membrane described above, at different temperatures. Results in Fig. 3(a) correspond to the CHR model and those in Fig. 3(b) to the SWE model. In both cases it becomes clear that for high enough voltages, most of the electric current is carried by water ions (transport numbers approach unity). Again, the SWE model prediction is less sensitive to temperature than that of the CHR model.

![Figure 3](image1.png)

Fig. 3. The quotient $(i_d/i_t)$ vs. the applied voltage for the temperatures considered in Fig. 2. Figure 3(a) corresponds to a CHR model and Fig. 3(b) to a SWE model, respectively.

Figure 4 refers to a model of anion-exchange membrane fouled with an adhered layer of electronegative impurities which acts as a cation-exchange membrane. The ratio $i_d/i_t$ is plotted against voltage, for different fixed-charge concentrations in the fouling layer. Water splitting is assumed to originate by the CHR model. As expected, the greater the concentration, the greater the water splitting effects (a reasonable result since the reaction constant depends exponentially on the electric field at the interface, and this field increases with fixed charge concentration). Typical values chosen for these calculations were $X_{np} = 1 M$, $d_{Rc} = 10^{-4}$ m, $T = 298$ K, $d_i = d_{Rf}/5$ (a fouling layer thinner than the anion-exchange membrane). The values of the fitting parameters were the same as used for the bipolar membranes considered in Fig. 2. The results obtained can be compared to the results predicted by the SWE model under similar conditions [6]. The fouling layer, even a relatively thin one, can cause significant water splitting effects provided that its fixed charge concentration is of the same order of magnitude as that of the membrane. Again, the CHR

![Figure 4](image2.png)

Fig. 4. The quotient $i_d/i_t$ vs. voltage for an anion-exchange membrane fouled with a cation-surface film. We employ a CHR model for water splitting. The curves are parametric in $X_{np}$. The thickness of the fouling film is $d_i = d_{Rf}/5$, and the temperature considered is $T = 298$ K.
model predicts stronger effects than the SWE model for low voltages [6].

Water splitting has been also observed in ion-exchange membranes without fouling [18,22,23]. For sufficiently high applied voltages the concentration polarization of the electrolyte in the boundary layer near the membrane–solution interface causes a strong decrease in the concentration of the ionic species in that layer; the expected consequence would be a limit in the electric current across the membrane, but the current carried by the \( \text{OH}^- \) and \( \text{H}^+ \) ions overcomes this theoretical limiting current. Experiments show that this phenomenon is particularly relevant in anion-exchange membranes where for high voltages almost the whole current is carried by water ions, while it is nearly negligible in cation-exchange membranes [18,22,23]. This can be seen as a clear evidence of the existence of specific chemical reactions at the membrane–solution interface, probably enhanced by the high electric fields occurring in that space–charge region, which are the cause of the excess of \( \text{OH}^- \) and \( \text{H}^+ \) ions [16,18]. A rough estimation of the electric field in the space–charge region as well as of the thickness of this region can be made by assuming that, for high enough applied voltages, there are no mobile ionic species in this zone [16]. Introduction of this assumption into the Poisson equation leads to:

\[
E = \frac{2FX_p}{\varepsilon_0 \varepsilon_r} V \quad (20)
\]

\[
\delta = \frac{2\varepsilon_0 \varepsilon_r}{FX_p} V \quad (21)
\]

where \( V \) is the potential difference across the space charge region. For a single anion exchange membrane, \( V \) can no longer be considered as the total applied voltage but only as a part of it, since the voltage drops in the boundary layers are quite significant. Thus, the model here developed cannot be directly applied to that system. Nevertheless, it can be shown that the CHR model for water splitting is consistent with the experimental results: by substituting the values for the fitting parameters \( \alpha \) and \( \varepsilon_r \) of eqn. (19) and taking \( X_p \approx 1M \) and \( V \approx 1V \) in eqns. (20) and (21), one obtains \( E \approx 9 \times 10^9 \) V/m and \( \delta \approx 20 \) Å for the electric field and the space–charge region thickness. Therefore, the enhancement of the forward rate constant in the reaction layer can be directly calculated from eqn. (15), and we find \( k_d/k_a \approx 7 \). If \( \alpha \) were of the order of \( 10^{-10} \) m, then the increase in the forward rate constant would be 50. These values seem to be consistent with the electric currents experimentally observed [16].

4. Discussion

Transport of four ions across a bipolar membrane has been analysed in terms of a simple analytical model based on an extension of the theory of charge carriers in solid state junctions [12]. Different assumptions regarding the mechanism of water dissociation can be introduced in the model and two of the most common in the literature have been studied. An exponential dependence of the rate of dissociation of water on the temperature is proposed and the results agree qualitatively with the experimental data reported by Zabolotskii et al. [19], within the voltage range considered. Generally speaking, it seems that the CHR model predictions are in better agreement with the experimental results than the SWE ones.

Let us note that the temperature dependence in the two models is very similar [because the factor \( (8b)^{-3/4} \) – see eqns. (12) and (13) – is hardly relevant when compared with the exponential dependence]. However, it seems unlikely that the SWE model may account for the “spreading” of the I–V curves as \( T \) increases. The reason may be found in the fact that the parameters involved in the SWE model, e.g. \( c_w \), \( E_{aw} \) and \( c_w \) take values limited by theory, while
in the CHR model, we have fitting parameters to be determined by experiment.

Also, the model worked out here can be of interest to describe ion transport and water splitting in fouled ion-exchange membranes. Finally, the extension of the present analysis to the polarization layer next to an anion-exchange membrane seems of interest because of the importance of reducing water splitting in electrodialytic systems. Further work is being carried out on this field.

Some limitations of the theory have been already pointed out [6,13]. Let us summarize the main restrictions implicitly or explicitly included in the model. First, Nernst–Planck equations, although widely admitted, may become questionable at a microscopic scale [25]. Recombination rates have been taken as non-dependent on the electric field, though the interface may be non-homogeneous. The dependence of the dissociation rate with temperature could be more complicated though reasonable results have been obtained with a $k_0^3$ incorporating two fitting parameters. These parameters are not directly accessible by experiment and it is not clear in what way they change with experimental conditions. However, the fact that the fitting parameters used lead to an increase in the dissociation rate constant similar to that observed, ensures the validity of, at least, their order of magnitude.

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List of symbols

- $A$: generation rate constant for water ions at a reference temperature (sec$^{-1}$)
- $\alpha$: length dimension parameter (m)
- $b$: dimensionless parameter
- $\beta_{N,P}$: parameters in ion-exchange layers N and P (m$^{-1}$)
- $c_{i,L,R}$: concentration of species $i$ in the bulk solutions L and R (mol/m$^3$)
- $\tilde{c}_{N,P}$: concentration of species $i$ in the ion exchange layers N and P (mol/m$^3$)
- $c_h$: concentration of water ions in the bulk solutions (mol/m$^3$)
- $c_s$: concentration of salt in the bulk solutions (mol/m$^3$)
- $c_w$: concentration of water in the bipolar membrane (mol/m$^3$)
- $D_{N,P}$: diffusion coefficient of species $i$ in the ion-exchange layers N and P (m$^2$/sec)
- $d_{i,L,R}$: ion exchange layer thicknesses (m)
- $\delta$: thickness of the neutral layer (m)
- $E$: electric field strength in the space-charge zone (V/m)
- $E_a$: activation energy (J/mol)
- $E_{sat}$: activation energy for the CHR model (J/mol)
- $E_{sw}$: activation energy for the SWE model (J/mol)
- $\varepsilon_0$: vacuum electric permittivity (Nm$^2$/C$^2$)
- $\varepsilon_r$: dielectric constant in the junction
- $F$: Faraday constant (C/mol)
- $I_1$: first-order Bessel function
- $i$: total electric current (A/m$^2$)
- $i_d$: electric current carried by the excess of water ions (A/m$^2$)
- $i_l$: limiting electric current (A/m$^2$)
- $J_i$: flux of species $i$ (mol/m$^2$.sec$^{-1}$)
- $k_d$: generation rate constant for water ions (sec$^{-1}$)
- $k_0^3$: generation rate constant for water ions in equilibrium (sec$^{-1}$)
- $k_0^7$: recombination rate constant for water ions (m$^3$/sec.mol$^{-1}$)
- $\lambda$: space-charge zone thickness (m)
- $\lambda_{N,P}$: thickness of the space-charge zone in the ion-exchange layers N and P (m)
- $n$: active sites concentration (mol/m$^3$)
\[ R \text{ gas constant (J/mol K)} \]
\[ T \text{ absolute temperature (K)} \]
\[ u_i \text{ mobility of species } i \text{ (m}^2\text{/sec-V)} \]
\[ X_{N,P} \text{ fixed charge concentration of the ion exchange layers N and P (mol/m}^3\text{)} \]
\[ x \text{ distance measured in direction of ion fluxes (m)} \]

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