Current Efficiency of an Ion-Exchange Membrane: Effect of Piecewise Continuous Fixed Charge Distribution

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The current efficiency η for the transport of ions through an ion-exchange membrane is analyzed theoretically. In particular, the effect of discretizing the fixed charges contained in the membrane into charged intervals on η is investigated. We show that if the applied current density I is low, a membrane with a continuous linear fixed charge distribution has a higher η than a membrane with evenly distributed charged intervals, and the larger the number of charged intervals the lower the η. If I is high, a membrane with randomly distributed charged intervals may have a higher η than that of a membrane with a continuous linear fixed charge distribution. It can be inferred that, as far as raising η is concerned, distributing fixed charges discretely and/or randomly in a membrane has no practical advantage.

Introduction

The amount and spatial variation of the fixed charges contained in an ion-selective membrane is known to have a significant effect on its performance. Reiss and Bassignana,[1] for example, showed that the current efficiency of a planar membrane with a sandwich type of fixed charge distribution has a higher current efficiency than that of a membrane with uniformly distributed fixed charges. Selvey and Reiss[2] showed that improving the performance of a membrane by distributing trigonometrically the fixed charges it contains is limited. This is also justified by Hsu and Ting in a recent study.[3] Increasing the degree of inhomogeneity of fixed charge distribution, however, does not always improve the performance of a membrane. By considering linear and exponential fixed charge distributions, Sokirko et al.[4] concluded that the improvement in the current efficiency of a membrane through varying fixed charge distribution occurred only for some level of applied current density, and the degree of improvement is related to current density. For cylindrical membranes, Hsu and Yang[5] also illustrated that raising the current efficiency of a membrane through distributing nonuniformly the fixed charges is conditional. Manzanares et al.[6] found that adopting a nonuniform fixed charge distribution can be disadvantageous to the current efficiency of a membrane. An attempt was made by Hsu and Ting[3] to correlate the current efficiency of a membrane with its fixed charge distribution by defining a parameter M_2. According to its definition, M_2 is the second moment of the adjusted scaled fixed charge distribution about the left liquid−membrane interface where the current flows into the membrane, normalized by the total amount of fixed charges. They showed that if the amount of fixed charges is fixed, and the direction of applied current is from the left of a membrane to its right, then M_2 might have a positive maximum and a negative minimum. The former occurs if all fixed charges are concentrated near the right liquid−membrane interface, and the latter occurs if all fixed charges are concentrated near the left liquid−membrane interface. Any other types of fixed charge distribution will have an M_2 between these two extremes, and M_2 vanishes if the fixed charges are distributed uniformly. Since M_2 is found to correlate closely with the current efficiency of a membrane, its can be used to predict the performance of the membrane.

Reported results in the literature almost always assume that fixed charges can be represented by a continuous function, that is, the length scale for the changes in fixed charge distribution is on the order of that for membrane,[6] and other possible types of fixed charge distribution are not considered.[7] This is mainly for a simpler mathematical treatment. In practice, it is more likely that fixed charges are distributed in a discrete manner, or piecewise continuous at best. Selvey and Reiss,[2] for example, pointed out that the ionic groups in a membrane are of discrete nature and can be simulated by trigonometric functions. Based on the result of small-angle X-ray scattering, it was postulated that sizable regions of length scale on the order 100 Å in which the ions are clustered exist in an organic polymer.[8−10] These lead to two immediate questions: (1) For the same total amount of fixed charges, is the performance of a membrane with a discrete fixed charge distribution better than that of a membrane with a continuous fixed charge distribution? (2) Is it advantageous to distribute randomly the fixed charges in a membrane?[6] Attempt has been made in the present study to answer these two questions.

Modeling

Referring to Figure 1, we consider a planar membrane of thickness W immersed in a 1:1 electrolyte solution. Let C_L and C_R be the concentrations of electrolyte on the left and on the right sides of the membrane, respectively. Without loss of generality, we consider a cation-selective membrane, i.e., the fixed charge is negative. The spatial distribution of fixed charge is piecewise continuous, with some portions of the membrane charged and the rest uncharged. The origin of the x-coordinate is located at the left liquid−membrane interface, and the direction of the applied current, I, is from the left of the membrane to its right. For simplicity, we assume that $C_L = C_R = C_0$ and the diffusivity of cation is the same as that of anion,

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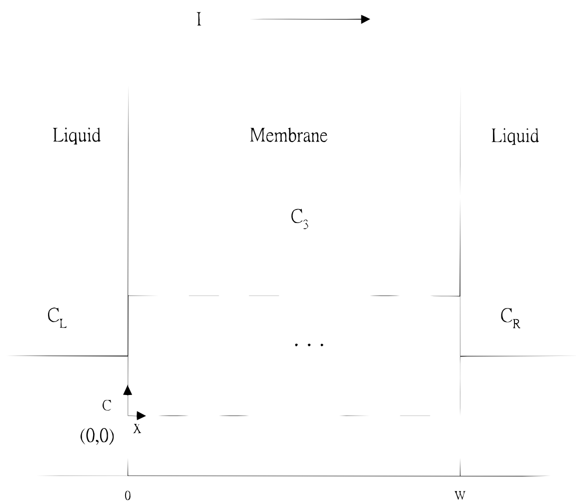

Figure 1. Schematic representation of the system under consideration. C_L and C_R are the left and the right bulk liquid concentrations, respectively, C_3 is the concentration of fixed charges, and W is the width of the membrane.

denoted as D. If the condition of local electroneutrality can be assumed, then it can be shown (see Appendix) that

$$\frac{dp}{dx} = \frac{p[h + g - (d\rho(x)/dx)] - h\rho(x)}{\rho(x) - 2p} \tag{1}$$

where $p = C_1/C_0$, $\rho = C_3/C_0$, $x = X/W$, $h = J_1W/DC_0$, $g = J_2W/DC_0$. C_1 and C_3 are, respectively, the molar concentrations of cation and fixed charge, J_1 and J_2 are, respectively, the fluxes of cation and anion. Suppose that Donnan equilibrium[7] is established at the liquid–membrane interface and the point at which the distribution of fixed charge is discontinuous.[1] In this case, eq 1 should be solved subject to the boundary conditions

$$p = p^0 = \frac{1}{2}\rho(0) + \left[\frac{1}{4}\rho(0)^2 + 1\right]^{1/2} \quad \text{at } x = 0 \tag{2}$$

$$p = p^1 = \frac{1}{2}\rho(1) + \left[\frac{1}{4}\rho(1)^2 + 1\right]^{1/2} \quad \text{at } x = 1 \tag{3}$$

where p^0 and p^1 are the values of p on the left and on the right margins of a plane on which the Donnan equilibrium is reached.

For specified i and $\rho(x)$, eq 1 should be solved subject to eqs 2 and 3, and the following expressions are used to evaluate current efficiency η (see Appendix):[6]

$$h = i\eta \tag{4}$$

$$g = i(\eta - 1) \tag{5}$$

In these expressions, $i = WI/FDC_0$ and $\eta = |J_1|/(|J_1| + |J_2|)$.

Results and Discussion

Two problems are discussed in the numerical simulation. First, if the total amount of fixed charges is fixed, is the current efficiency of a membrane with a discrete fixed charge distribution higher than that of a membrane with a continuous fixed charge distribution? Second, is the current efficiency of a membrane with a random discrete fixed charge distribution is higher than that of a membrane with a uniform discrete fixed charge distribution? To answer the first question, a membrane is divided into a certain number of uncharged regions and a certain number of charged regions. Each region has the same width, and the fixed charges are distributed uniformly in each charged interval. Every two charged regions are separated by an uncharged region. For simplicity, we assume that the regions next to the left liquid–membrane interface and to the right liquid–membrane interface are charged. Therefore, if there are N charged regions, then there will be $(N - 1)$ uncharged regions. For each N, the parameter M_2 defined below is evaluated[3]

$$M_2 = \frac{1}{\gamma}\int_0^1[\rho(x) - \gamma]x^2dx \tag{6}$$

where γ is the scaled mean fixed charge concentration defined by

$$\gamma = \int_0^1\rho(x)dx \tag{7}$$

Since the scaled width of the membrane is unity, γ is also the scaled total amount of fixed charges. It can be shown (see Appendix) that for the present case $\gamma = 1$ and $M_2 = (N - 1)/[3(2N - 1)^2]$. Table 1 and Figure 2 show the variation in the current efficiency η as a function of the number of charged regions, reflected by M_2, at two levels of scaled current density.

TABLE 1: Variation in the Current Efficiency of a Membrane η as a Function of the Number of Charged Regions N at Two Levels of Applied Current Density[a]

N	η ($i = 5$)	η ($i = 10$)	η_{lin} ($i = 5$)	η_{lin} ($i = 10$)	M_2
2	0.7181	0.7313	0.7300	0.7364	0.0370
3	0.7141	0.7218	0.7283	0.7328	0.0267
4	0.7122	0.7175	0.7272	0.7306	0.0204
5	0.7111	0.7151	0.7265	0.7292	0.0165
6	0.7104	0.7136	0.7260	0.7282	0.0138
7	0.7099	0.7125	0.7257	0.7276	0.0118
8	0.7095	0.7118	0.7254	0.7271	0.0104
9	0.7092	0.7112	0.7252	0.7267	0.0092
10	0.7090	0.7108	0.7251	0.7264	0.0083
15	0.7083	0.7095	0.7246	0.7255	0.0056
20	0.7080	0.7089	0.7243	0.7250	0.0042
25	0.7078	0.7085	0.7242	0.7247	0.0033
30	0.7077	0.7083	0.7241	0.7246	0.0028
35	0.7076	0.7081	0.7240	0.7244	0.0024
40	0.7076	0.7080	0.7240	0.7243	0.0021
50	0.7075	0.7080	0.7240	0.7242	0.0017

[a] η_{lin} denotes the current efficiency of a membrane with a continuous linear fixed charge distribution. Parameters used are $\gamma = 1$, $p(x = 0) = n(x = 0^-) = p(x = 1^+) = n(x = 1^+) = 1$. The total amount of fixed charges remains at constant in each case.

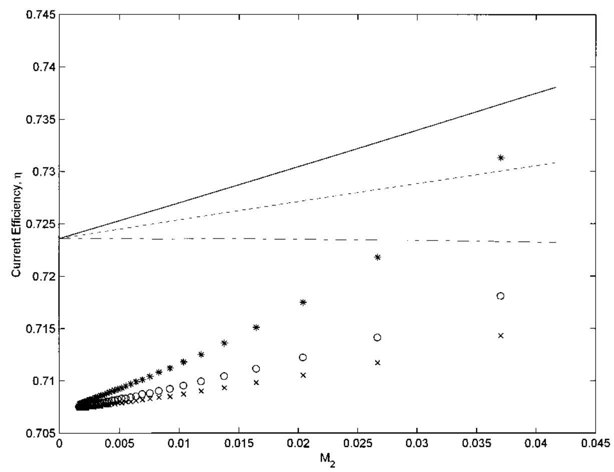

Figure 2. Variation in the current efficiency, η, as a function of parameter M_2 at two levels of scaled current density i. Symbols correspond to (even) piecewise continuous distributions with up to $N = 50$ charged regions with $i = 10$, *; $i = 5$, ○; $i = 10^{-6}$, ×. Lines are the results for the case of continuous linear fixed charge distribution with $i = 10$, —, $i = 5$, - - -, and $i = 10^{-6}$, —•—. Key: $\gamma = 1$, $p(x = 0) = n(x = 0^-) = p(x = 1^+) = n(x = 1^+) = 1$.

For comparison, the results for the case where a membrane has the following continuous linear fixed charge distribution are also illustrated:

$$\rho(x) = \alpha + \beta x \tag{8}$$

where α and β are constant. The results for the case $i \to 0$ are also presented in Figure 2 for reference. In Table 1 the total amount of fixed charges, the thickness of the membrane, and the bulk concentration of electrolytes remain constant. Note that for the case of linear fixed charge distribution each M_2 corresponds to a different membrane, and β can be expressed in terms of α.[3] Also, $M_2 = 0$ corresponds to a homogeneous membrane. Note that in Table 1 if i exceeds about 14, the concentration of ions in the membrane phase becomes negative for $N = 2$; this critical value increases with N. Apparently, i should not exceed the corresponding critical value for each N. Table 1 reveals that η decreases with the increase in the number of charged regions. Since η approaches a constant value as the number of charged regions increases, this implies that if the total amount of fixed charges is fixed, the more the fixed charges are discretely distributed, the less satisfactory its performance. As can be seen from Figure 2, for linearly distributed fixed charges η increases with M_2, which is a measure for the degree of inhomogeneity of fixed charge distribution for the present case. This is consistent with the result of Hsu and Ting.[3] For a lower applied current density, the current efficiency for a membrane with a linearly distributed fixed charge is higher than that for a membrane with a discrete fixed charge distribution. For a higher current density, however, it is possible that distributing fixed charges in a finite number of charged regions may lead to a higher current efficiency than distributing them in a continuous manner. This is why a membrane with a sandwich-type fixed charge distribution proposed by Reiss and Bassignana,[1] performs better than a membrane with a uniform fixed charge distribution. It should be pointed out that using the present piecewise continuous model to predict the value of η as $M_2 \to 0$ is inappropriate. This is because, although the present model can be used to simulate a discrete fixed charge distribution, the number of charged regions N has an upper limit. This is because if N is too large, the assumption of Donnan equilibrium becomes invalid. Also, in our previous study,[3] in which only continuous fixed charge distributions are considered, η and M_2 are found to correlate nicely. At a glance of Figure 2, one may have the impression that $\eta = \eta(M_2)$ is no longer valid for the present case. This is not the case because, for a fixed M_2, η (continuous fixed charge distributions) $\cong$ η (piecewise continuous fixed charge distributions), the difference between the two is on the order of 1%. In general, the correlation coefficient for the relation $\eta(M_2)$ for a continuous fixed charge distributions is larger than that for a piecewise fixed charge distributions.

To answer the second question, five charged regions and three uncharged regions are randomly allocated in a membrane. There are 35 different combinations, and for each combination M_2 and η are evaluated. Figures 3 through 5 show the variation of η as a function of M_2 for $i = 1$, 5, and 10, respectively. The results for linearly distributed fixed charges are also presented for comparison. For reference, the results for the case $i \to 0$ are also shown in Figure 3. Figures 3 and 4 show that if the current density is low, distributing randomly the charged regions in a membrane has no advantage. As can be seen from Figure 5, however, if the applied current density is high, distributing randomly the charged regions may lead to a higher current efficiency. This occurs, however, at a large M_2; that is, the charged regions are concentrated near the rightmost liquid−membrane interface. This is consistent with the result of Hsu and Ting.[3] Note that, as mentioned previously, although η (continuous fixed charge distribution) $\cong$ η (piecewise continuous fixed charge distribution), the former is found to be consistently

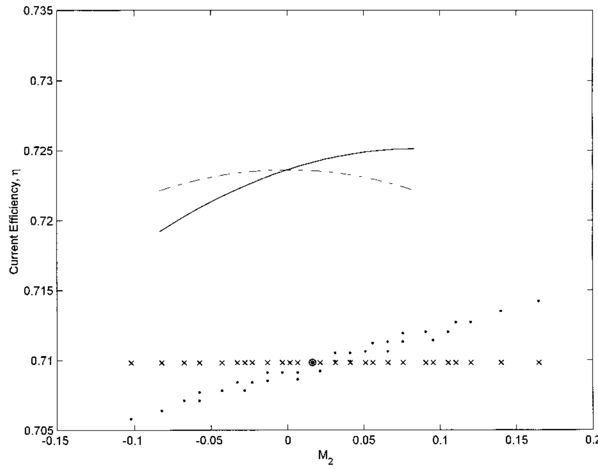

Figure 3. Variation in the current efficiency, η, as a function of parameter M_2 for $i = 1$, ●, and $i = 10^{-6}$, ×. The even distribution considered in Figure 2 for $N = 5$ has been marked with an asterisk * for $i = 1$ and with ○ for $i = 10^{-6}$. Lines are the results for the case of continuous linear fixed charge distribution with $i = 1$, —, and $i = 10^{-6}$, —•—. Key: same as Figure 2.

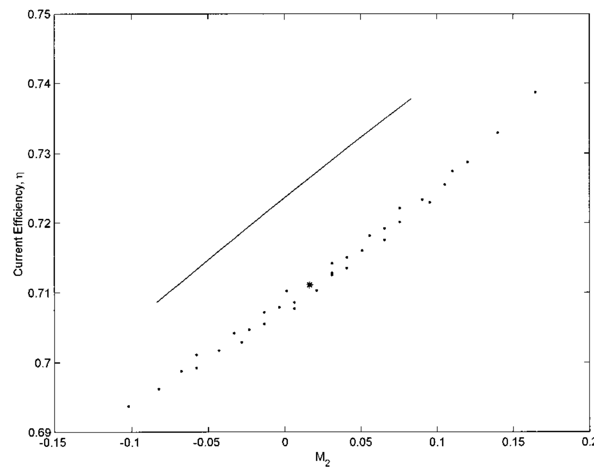

Figure 4. Variation in the current efficiency, η, as a function of parameter M_2 for the case of Figure 3, except $i = 5$.

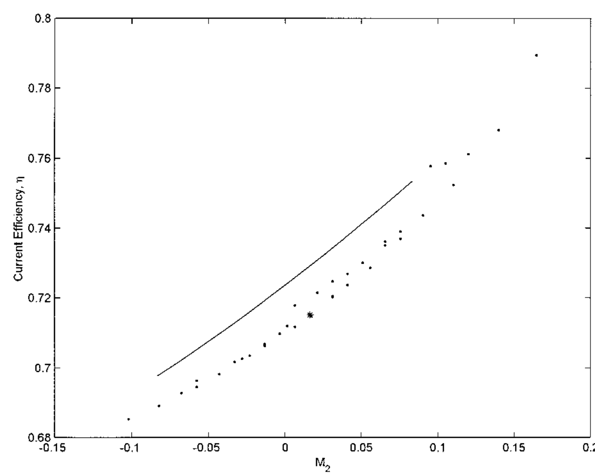

Figure 5. Variation in the current efficiency, η, as a function of parameter M_2 for the case of Figure 3, except $i = 10$.

higher than the latter. According to Manzanares et al.,[6] current efficiency is inversely related to the average coion concentration in a membrane. Due to the presence of uncharged regions, the membrane with the piecewise continuous fixed charge distribution has a higher average coion concentration than the membrane with the linear fixed charge distribution (which has a scaled minimum fixed charge distribution of 0.5), and, therefore, the current efficiency of the former is lower than that of the latter. Also, for the case $i \to 0$, since the average concentration of coins within a membrane remains unchanged under the randomization process, the current efficiency is the same as M_2 varies, as shown in Figure 3.

It should be mentioned that the presence of the boundary layer near liquid–membrane interface plays a much more significant role than the distribution of fixed charge in the estimation the performance of a membrane,[4,12] and a more rigorous analysis should take this effect into account.

In summary, we conclude that the effect of fixed charge distribution on the performance of a membrane is closely related to a parameter, which characterizes the spatial variation of fixed charges. On the basis of the results obtained for discretizing fixed charges into a finite number of charged regions, it can be inferred that, as far as raising the current efficiency is concerned, distributing fixed charges discretely and/or randomly in a membrane has no practical advantage.

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Appendix

The transport of ion species is governed by the Nernst–Planck equation[11]

$$J_j = -D_j\left[\frac{\mathrm{d}C_j}{\mathrm{d}X} + (-1)^{j+1}\frac{q}{k_B T}C_j\frac{\mathrm{d}\psi}{\mathrm{d}X}\right] \quad j = 1, 2 \qquad \text{(A1)}$$

where C_j, D_j, and J_j, represent, respectively, the molar concentration, diffusivity, and flux of ion species j ($j = 1$, cation; $j = 2$, anion); q, k_B, and T are the elementary charge, the Boltzmann constant, and the absolute temperature, respectively. Suppose that the condition of local electroneutrality is applicable, that is

$$C_1 = C_2 + C_3 \quad 0 < X < W \qquad \text{(A2)}$$

The density of the applied current, I, can be expressed as

$$I = F(J_1 - J_2) \qquad \text{(A3)}$$

where F is the Faraday constant. For the cases $C_L = C_R = C_0$ and $D_1 = D_2 = D$, eqs A1 through A3 can be rewritten in the following scaled form:

$$h = -\frac{\mathrm{d}p}{\mathrm{d}x} - p\frac{\mathrm{d}\phi}{\mathrm{d}x} \qquad \text{(A4)}$$

$$g = -\frac{\mathrm{d}n}{\mathrm{d}x} + n\frac{\mathrm{d}\phi}{\mathrm{d}x} \qquad \text{(A5)}$$

$$p = n + \rho(x) \qquad \text{(A6)}$$

$$i = h - g \qquad \text{(A7)}$$

where i is the scaled current density, x, p, ρ, h, and g are defined in the text, $n = C_2/C_0$, and $\phi = (q\psi/k_BT)$. The current efficiency of a membrane η can be expressed as

$$\eta = \frac{|h|}{|h| + |g|} \qquad \text{(A8)}$$

Solving eqs A7 and A8 for h and g yields eqs 4 and 5 in the text. Equations A4 through A6 lead to eq 1 in the text.

For the case where N charged regions are evenly distributed across a membrane we have $\rho = (2N - 1)/\mathrm{N}$ in each region. Then

$$\begin{aligned}\gamma &= \int_0^1 \rho(x)\mathrm{d}x \\ &= \frac{2N-1}{N}\left[\left(\frac{1}{2N-1} - 0\right) + \left(\frac{3}{2N-1} - \frac{1}{2N-1}\right) + \ldots + \left(\frac{2N-1}{2N-1} - \frac{2N-2}{2N-1}\right)\right] \\ &= \frac{1}{N}[(1 + 3 + 5 + \ldots + (2N-1)) - (2 + 4 + 6 + \ldots + (2N-2))] \\ &= \frac{1}{N}[N^2 - N(N-1)] \\ &= 1 \end{aligned} \qquad \text{(A9)}$$

Therefore, eq 6 yields

$$\begin{aligned} M_2 &= \frac{1}{\gamma}\int_0^1[\rho(x) - \gamma]x^2\mathrm{d}x = \int_0^1 \rho(x)x^2\mathrm{d}x - \int_0^1 x^2\mathrm{d}x \\ &= \frac{1}{3}\left(\frac{2N-1}{N}\right)\left[\left(\frac{1}{2N-1}\right)^3 - 0 + \left(\frac{3}{2N-1}\right)^3 - \left(\frac{2}{2N-1}\right)^3 + \ldots + \left(\frac{2N-1}{2N-1}\right)^3 - \left(\frac{2N-2}{2N-1}\right)^3\right] - \frac{1}{3} \\ &= \frac{1}{3N(2N-1)^2}\{[1^3 + 3^3 + \ldots + (2N-1)^3] - [2^3 + 4^3 + \ldots + (2N-2)^3]\} - \frac{1}{3} \\ &= \frac{1}{3N(2N-1)^2}[N(4N-3)] - \frac{1}{3} \\ &= \frac{N-1}{3(2N-1)^2} \end{aligned} \qquad \text{(A10)}$$

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