

Ion-exchange funneling in thin-film coating modification of heterogeneous electro dialysis membranes

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Inexpensive highly permselective heterogeneous ion-exchange membranes are prohibitively highly polarizable by a dc current for being used in electro dialysis. According to recent experiments, polarizability of these membranes may be considerably reduced by casting on their surface a thin layer of crosslinked polyelectrolyte, slightly charged with the same sign as the membrane's charge. The present paper is concerned with this effect. Concentration polarization of a permselective heterogeneous ion-exchange membrane by a dc current is determined by geometric factors, such as, the typical size of the ion-permeable "gates" at the membrane surface relative to the separation distance between them and the diffusion layer thickness. The main quantitative characteristic of polarizability of a heterogeneous membrane is its voltage/current curve with its typical saturation at the limiting current, which is lower than that for a homogeneous membrane. In the present study we modify the previously developed two-dimensional model of ionic transport in a diffusion layer at a heterogeneous ion-exchange membrane by including into consideration a homogeneous ion-exchange layer adjacent to the membrane surface. A numerical solution of the respective boundary value problem shows that, indeed, adding even a very thin and weakly charged layer of this kind increases the value of the limiting current, to that of a homogeneous membrane. What differs, for different values of coating parameters, is the form of the voltage/current curves but not the value of the limiting current, namely: the thinner is the coating and the lower the fixed charge density in it, the "slower" is the approach of the limiting current. In order to explain this feature, a simple limiting model of modified membrane is derived from the original two-layer model. In this limiting model, asymptotically valid for a thin coating, solution of the ionic transport equations in it is replaced, via a suitable averaging procedure, by a single nonlinear boundary condition for the membrane/solution interface. Rigorous analysis shows that the aforementioned property of the limiting current is an exact mathematical feature of this limiting model, when the underlying physical phenomenon is the funneling of counterions by the charged layer from the impermeable parts of the membrane towards the "entrance gates." An approximate analytical solution, developed for this model, compares well with the exact numerical one.

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I. INTRODUCTION

Electro dialysis is an ion separation (e.g., desalination) process based upon passing a direct electric current through an electrolyte solution flanked by a few hundred of microns thick charge selective (permselective) polymer films—ion-exchange membranes. Two types of ion-exchange membranes are distinguished—homogeneous and heterogeneous ones.

Homogeneous membranes, consisting of cross-linked polyelectrolyte, are prohibitively expensive for their practical use in a large scale desalination by electro dialysis. On the other hand, the use for this purpose of inexpensive heterogeneous membranes, made of tens of microns sized ion exchange beads sealed in a neutral polymer matrix, is largely impaired by their prohibitively high polarizability compared to that of a homogeneous membrane. By this we mean that the differential dc resistance of a heterogeneous membrane with the adjacent electrolyte layers increases more rapidly with the increase of current than that of a homogeneous membrane. This increase is the essence of concentration polarization (CP) in a solution layer adjacent to a charge selective body (ion-exchange membrane, electrode) under the passage of a dc current. Electrolyte concentration gradient

that develops, results in a typical nonlinear steady state voltage/current (VC) dependence, schematically depicted in Fig. 1. The following three regions are typically distinguishable in such a curve. The low current Ohmic region I is followed by a plateau with a much lower slope [region II, the limiting current (LC)]. Inflection of the VC curve at the plateau is followed by the "overlimiting" region III. Transition

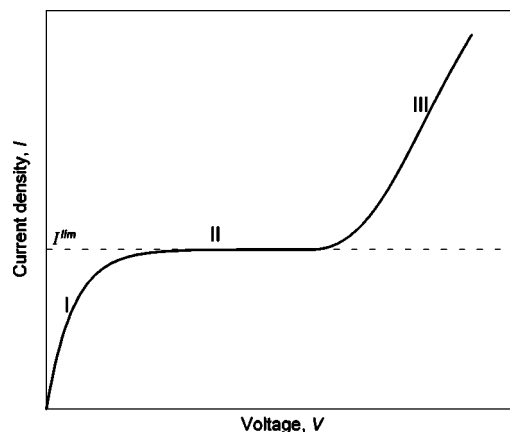


FIG. 1. Sketch of a typical dimensionless voltage/current curve of a cation-exchange membrane.

to the overlimiting regime is accompanied by the appearance of a low-frequency excess electric noise. For a recent discussion of the overlimiting phenomena the interested reader is referred to Ref. [1]. In the current context, we are concerned with the classical “underlimiting” CP regions I and II.

Higher polarizability of a heterogeneous membrane compared to a homogeneous one amounts to a lower LC at the former than at the latter. Yet, the recent experiments suggest that polarizability of heterogeneous membranes may be considerably reduced by casting on their surface a thin layer of a cross-linked polyelectrolyte (ion-exchange coating), slightly charged with the same sign as the membrane’s charge [2]. Our present theoretical study is concerned with this effect.

Polarizability of a permselective heterogeneous ion-exchange membrane by a dc current is determined by geometric factors, such as, the typical size of the ion-permeable “gates” at the membrane surface in relation to the separation distance between them and the diffusion layer thickness, as modeled by an earlier two-dimensional (2D) theory [3].

In the present study we modify this theory by including into consideration a homogeneous ion-exchange layer adjacent to the membrane surface (Sec. II). A numerical solution of the respective boundary value problem (BVP) in Sec. III shows that, indeed, even a very thin and slightly charged coating of this kind increases the value of the limiting current to that of a homogeneous membrane. (What differs, for varying coating’s parameters, is the shape of the VC curves but not the value of the LC, namely: the thinner is the coating and the lower the fixed charge density in it, the “slower” is the approach of the limiting current.)

In order to explain this feature, a simple limiting model of modified membrane is derived from the original two-layer description (Sec. IV). In this limiting model, asymptotically valid for a thin coating, solution of the ionic transport equations in it is replaced, via a suitable averaging procedure, by a single nonlinear boundary condition for the membrane/solution interface. Rigorous analysis shows that the aforementioned property of the limiting current is an exact mathematical feature of this limiting model [4], when the underlying physical phenomenon is the funneling of counterions by the charged layer from the impermeable parts of the membrane towards the “entrance gates.” Approximate analytical solution, developed for this model, compares well with the exact numerical one.

II. ELECTRODIFFUSION IN A TWO-DIMENSIONAL PERIODICITY CELL AT A MODIFIED HETEROGENEOUS MEMBRANE

Let us consider a diffusion layer of univalent electrolyte adjacent to a charged coating layer on a flat heterogeneous membrane. Let the dimensional thickness of the diffusion layer be $\tilde{\delta}$ and that of the charged layer $\tilde{\varepsilon}$. Confining ourselves to a two-dimensional case, let us model the heterogeneous membrane/coating interface as a periodic array of conductive, ideally cation permselective and insulating strips of half-width \tilde{h} and $l-\tilde{h}$, respectively (here l is the spatial period, used below for scaling). Let us direct the \tilde{x} axis normal

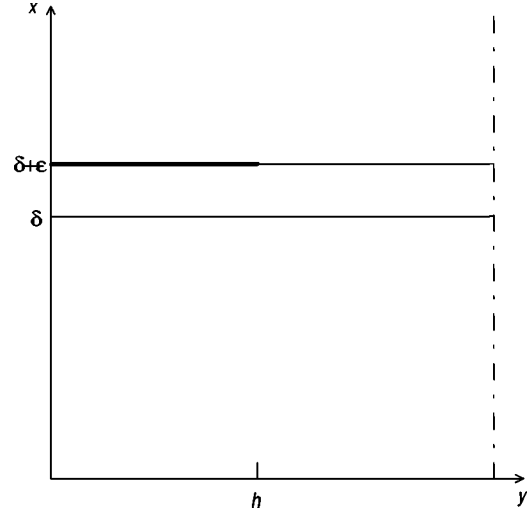


FIG. 2. Sketch of the problems’ geometry.

to the interface, with the origin at the outside, “bulk” edge of the diffusion layer, and \tilde{y} parallel to the interface and perpendicular to the strips at it. Thus, ion transfer in the diffusion layer and the coating may be reduced to that in a single periodicity cell confined by the membrane/coating interface, bulk edge of the diffusion layer and the two symmetry planes $\tilde{y}=0, l$ (middle of the conductive and insulating strips, respectively, as illustrated in Fig. 2).

In terms of natural dimensionless variables, the two-dimensional Nernst-Planck equations for locally electroneutral steady-state electrodiffusion of cations and anions in the diffusion layer ($0 < x < 1, 0 < y < 1$) read

$$\nabla(\nabla c + c\nabla\varphi) = 0, \quad (1)$$

$$\nabla(\nabla c - c\nabla\varphi) = 0. \quad (2)$$

Hereon the untilded notations stand for the dimensionless variables, whereas the tilded ones stand for their dimensional counterparts. Thus, $c = \tilde{c}/c_0$ is the dimensionless electrolyte concentration, where c_0 , employed for scaling, is the bulk concentration maintained constant at the outside edge of the diffusion layer; $\varphi = e\tilde{\varphi}/kT$ is the electric potential (e is the charge of proton, k is the Boltzmann constant, and T is the absolute temperature), $x = \tilde{x}/l$, $y = \tilde{y}/l$ are the dimensionless coordinates.

By addition and subtraction, Eqs. (1),(2) are conveniently rewritten as the steady state diffusion (Laplace) and current continuity equations, respectively,

$$\Delta c = 0, \quad (3)$$

$$\nabla(c\nabla\varphi) = 0. \quad (4)$$

Similarly to Eqs. (1),(2), the electrodiffusion equations for the interior of ion-exchange coating ($\delta < x < \delta + \varepsilon, 0 < y < 1$) are

$$\nabla(\nabla p + p\nabla\varphi) = 0, \quad (5)$$

$$\nabla(\nabla n - n \nabla \varphi) = 0, \quad (6)$$

where $p = \tilde{p}/c_0$, $n = \tilde{n}/c_0$ are the cations and anion concentrations, respectively, related by the local electroneutrality condition

$$p = n + N. \quad (7)$$

Here $N = \tilde{N}/c_0$ is the fixed charge concentration in the coating, assumed hereon constant. For a cation-exchange membrane $N = \text{const} > 0$.

Continuity of the ionic fluxes and the electrochemical potentials at the coating/electrolyte interface ($x = \delta, 0 < y < 1$) imply

$$(p_x + p \varphi_x)|_{x=\delta+0} = (c_x + c \varphi_x)|_{x=\delta-0}, \quad (8)$$

$$(n_x - n \varphi_x)|_{x=\delta+0} = (c_x - c \varphi_x)|_{x=\delta-0}, \quad (9)$$

$$(\ln p + \varphi)|_{x=\delta+0} = (\ln c + \varphi)|_{x=\delta-0}, \quad (10)$$

$$(\ln n - \varphi)|_{x=\delta+0} = (\ln c - \varphi)|_{x=\delta-0}. \quad (11)$$

In Eqs. (8),(9), equal ionic diffusivities for the solution and the coating have been assumed for simplicity.

Simplest relevant boundary conditions at the heterogeneous membrane/coating interface ($x = \delta + \varepsilon, 0 < y < 1$) pertain to the galvanostatic regime of operation, assuming a uniform distribution of current over the cation permeable portion of the interface. These boundary conditions read

$$(p_x + p \varphi_x)|_{x=\delta+\varepsilon} = \begin{cases} -i, & 0 < y < h, \\ 0, & h < y < 1, \end{cases} \quad (12)$$

$$(n_x - n \varphi_x)|_{x=\delta+\varepsilon} = 0. \quad (13)$$

Here i is the constant dimensionless current density through the conductive strip of dimensionless half-width $h = \tilde{h}/l$ (def $I = ih$ is the average current density through the membrane). Boundary condition (13) pertains to impermeability for cations (anions) of both the insulating and conductive portion of the ideally cation permselective heterogeneous membrane under consideration. For the symmetry planes $y = 0, 1, 0 < x < \delta + \varepsilon$ we have

$$p_y|_{y=0,1} = 0, \quad (14)$$

$$n_y|_{y=0,1} = 0, \quad (15)$$

$$c_y|_{y=0,1} = 0, \quad (16)$$

$$\varphi_y|_{y=0,1} = 0. \quad (17)$$

Finally, the boundary conditions at the outer bulk edge of the diffusion layer $x = 0, 0 < y < 1$ are

$$c(0, y) = 1, \quad (18)$$

$$\varphi(0, y) = 0. \quad (19)$$

[The normalization condition (19) merely specifies the arbitrary constant in the definition of the electric potential.]

We point out first that the impermeability of the membrane for anions, Eq. (13), together with Eqs. (2),(6) implies

$$\varphi(x, y) = \ln c(x, y). \quad (20)$$

Furthermore, for $\varepsilon = 0$ (or $N = 0$) the BVP (3)–(20) is reduced to that for an unmodified heterogeneous membrane. This problem has been studied in Ref. [3]. The main results of this study may be summarized as follows. For $\varepsilon = 0$, $c(x, y)$ is found by separation of variables as

$$c(x, y) = 1 - \frac{I}{2}x - \frac{I}{4\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \frac{\sinh k \pi x}{\cosh k \pi \delta} \sin k \pi h \cos k \pi y. \quad (21)$$

Expression (21) yields the limiting current density at the heterogeneous membrane, corresponding to $c(\delta, 0) = 0$, as

$$I^{\text{lim}} = \frac{1}{\frac{\delta}{2} + \frac{1}{\pi^2 h} \sum_{k=1}^{\infty} \frac{1}{k^2} \tanh k \pi \delta \sin k \pi h}. \quad (22)$$

For $h \ll 1, \delta \gg 1$ expressions (21),(22) yield, to the leading order,

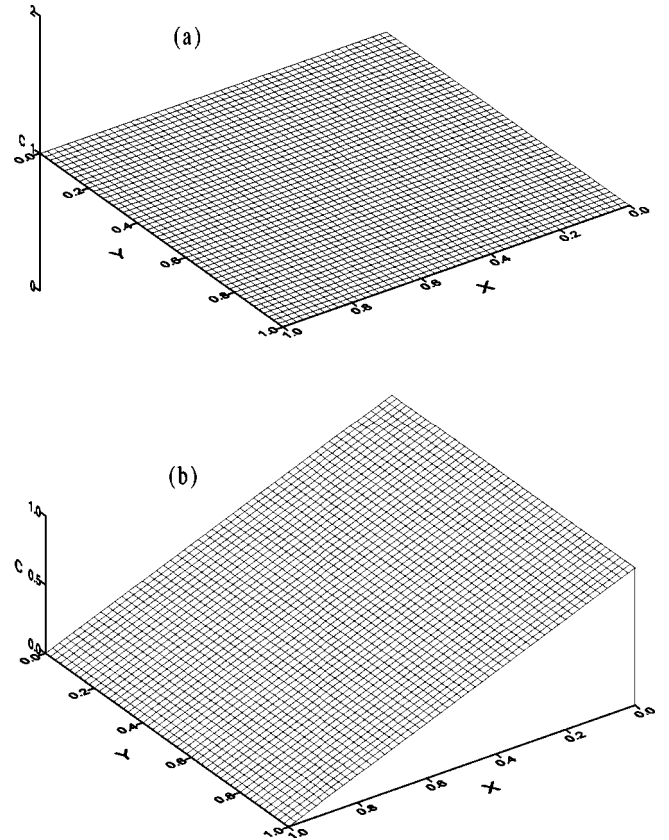


FIG. 3. 2D concentration distribution at a homogeneous membrane $\delta = 1, h = 1$ (a) $I = 0$; (b) $I = I_h^{\text{lim}} = (2/\delta) (= 2)$.

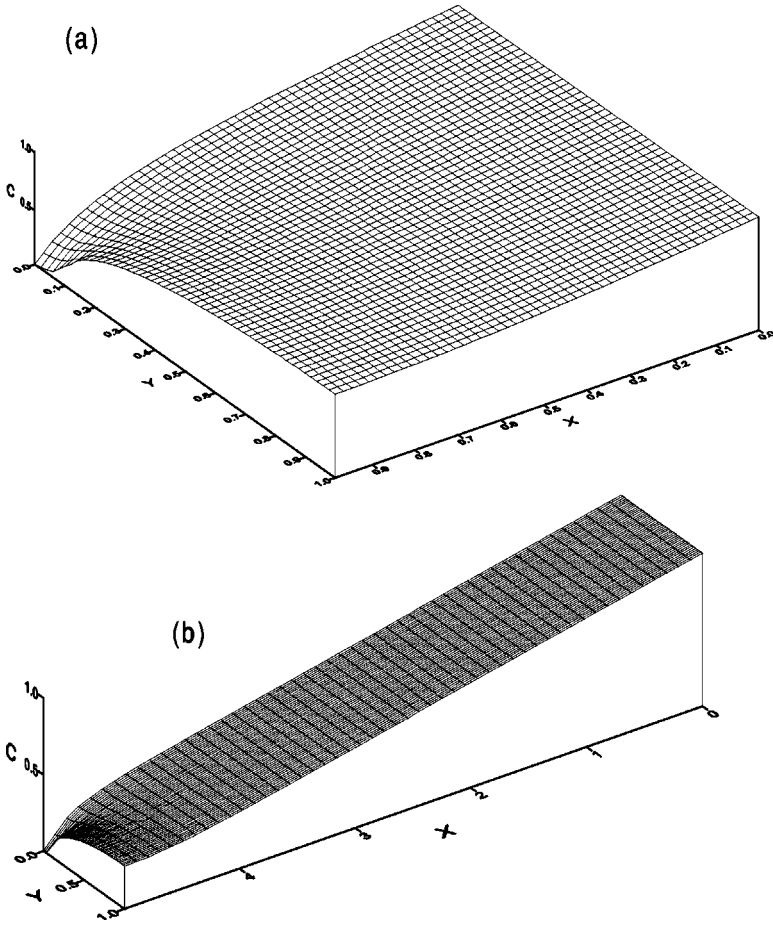


FIG. 4. 2D concentration distribution at a heterogeneous membrane (a) $\delta=1$, $h=0.1$, $I=I^{\text{lim}}=0.84$ ($I_h^{\text{lim}}=2/\delta=2$); (b) $\delta=5$, $h=0.1$, $I=I^{\text{lim}}=0.314$ ($I_h^{\text{lim}}=2/\delta=0.4$).

$$\begin{aligned}
 c^0(x,y) = & 1 - \frac{I}{2}x + \frac{I}{2\pi} \ln \frac{1 - 2e^{\pi(x-\delta)} \cos \pi y + e^{2\pi(x-\delta)}}{\pi^2(\delta-x)^2 + \pi^2 y^2} \\
 & + \frac{I}{4\pi} \left[\frac{y}{h} \ln \frac{(\delta-x)^2 + (h+y)^2}{(\delta-x)^2 + (h-y)^2} + \ln \{ [(\delta-x)^2 \right. \\
 & \left. + (h-y)^2][(\delta-x)^2 + (h+y)^2] \} + 2 \frac{\delta-x}{h} \right. \\
 & \left. \times \left(\arctan \frac{h-y}{\delta-x} + \arctan \frac{h+y}{\delta-x} \right) + 4(\ln \pi - 1) \right], \quad (23)
 \end{aligned}$$

$$I_0^{\text{lim}} = \frac{1}{\delta/2 - \frac{1}{\pi} [\ln(\pi h) - 1]}. \quad (24)$$

The full BVP (3)–(20) has been solved numerically by finite differences. The results are illustrated in Figs. 3–7.

To set the background, we begin in Figs. 3 and 4 with some results for the unmodified membrane, starting in Fig. 3 with a two-dimensional concentration distribution in the diffusion layer at a homogeneous membrane for zero and limiting current, respectively. In Fig. 4 the same distributions are presented for the unmodified heterogeneous membranes at the limiting current for two different diffusion layer thick-

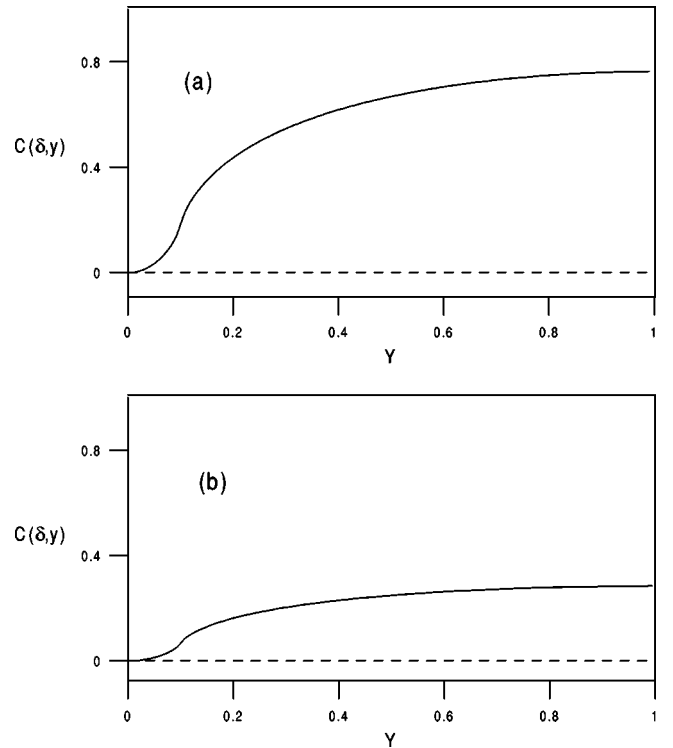


FIG. 5. Interface concentration profiles. —, homogeneous membrane ($h=1$); - - -, heterogeneous membrane ($h=0.1$). (a) $\delta=1$; —, $I=I_h^{\text{lim}}=2$; - - -, $I=I^{\text{lim}}=0.84$; (b) $\delta=5$; —, $I=I_h^{\text{lim}}=0.4$, - - - $I=I^{\text{lim}}=0.314$.

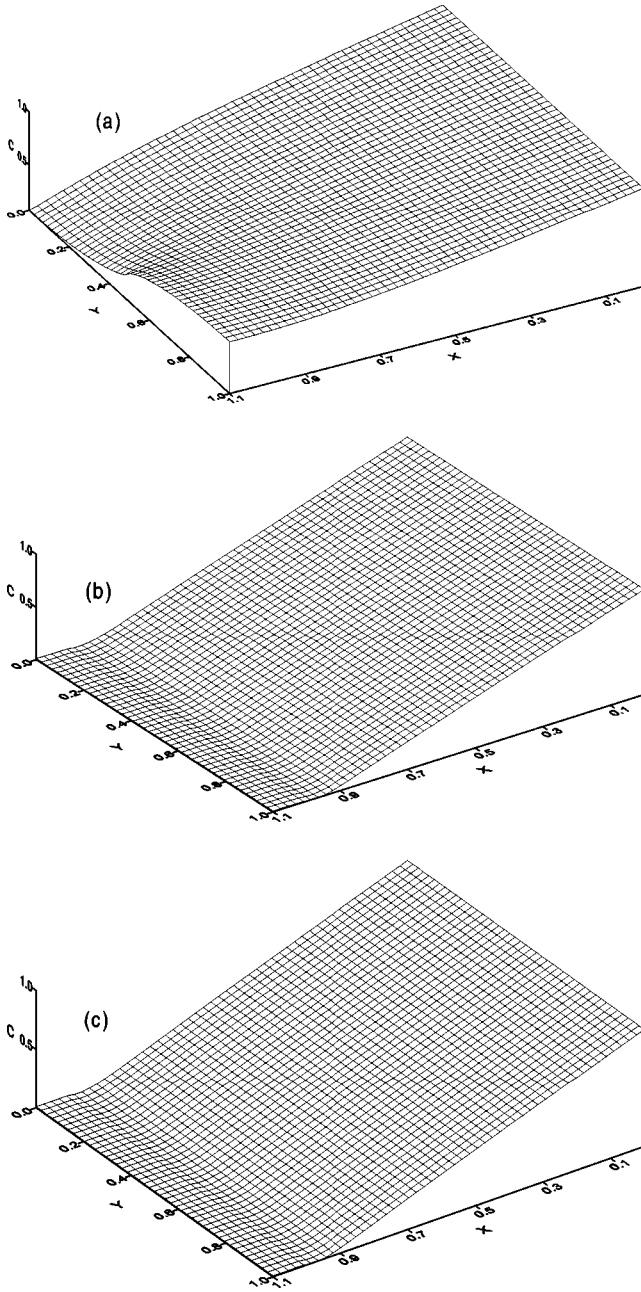


FIG. 6. Interface concentration profiles for a coated membrane at the limiting current. (a),(b) parameters as in Figs. 5(a) and 5(b), respectively, (c) homogeneous membrane at the limiting current ($\delta=1, h=1$).

nesses. It is observed that the thicker the diffusion layer is, the closer the concentration distribution is to that at a homogeneous membrane. This is also illustrated in Fig. 5 by the respective interface concentration profiles at the limiting current. [For a given heterogeneity (h), the thicker the diffusion layer is (the larger δ is), the flatter the interface concentration profile is and, correspondingly, the closer the value of the limiting current is to that for a homogeneous membrane.]

Against this background, the striking effect of coating consists of a virtually complete flattening of the concentration distribution and of the interface concentration profile already for a minor coating layer thickness and charge, and,

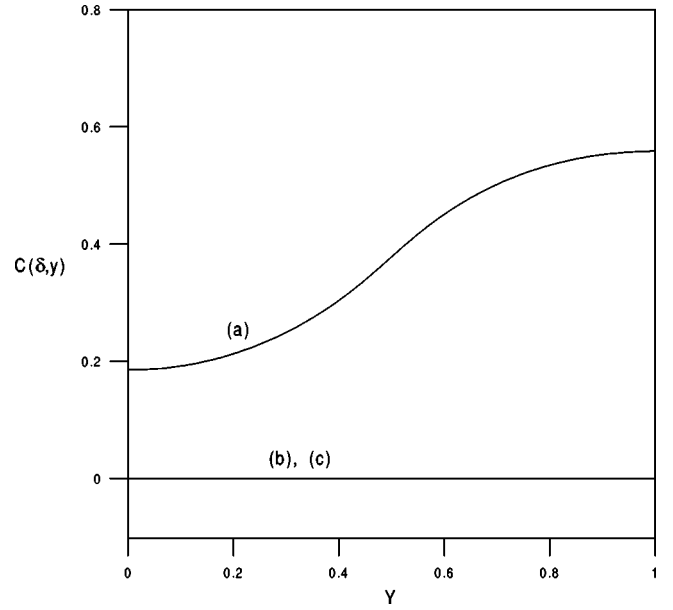


FIG. 7. 2D concentration distribution at a modified membrane. (a) Zero coating charge, i.e., unmodified heterogeneous membrane with a thicker diffusion layer $\varepsilon=0.1$, $N=0$, $h=0.5$, $\delta=1$, $I=I^{\text{lim}}=1.19$. (b) Charge coating $\varepsilon=0.1$, $N=0.01$, $h=0.5$, $\delta=1$, $I=I^{\text{lim}}=2$. (c) Homogeneous membrane $\varepsilon=0.1$, $N=0.01$, $h=1$, $\delta=1$, $I^{\text{lim}}=2$.

respectively, of the bringing the limiting current to a value typical of a homogeneous membrane. This is illustrated in Figs. 6–7, for $\varepsilon=0.1$, $N=0$, $h=0.5$, $\delta=1$ [Figs. 6(a) and 7(a), unmodified heterogeneous membrane, $I^{\text{lim}}=1.19$], $\varepsilon=0.1$, $N=0.01$, $h=0.5$, $\delta=1$ [Figs. 6(b) and 7(b), modified heterogeneous membrane, $I^{\text{lim}}=2.0$], $\varepsilon=0.1$, $h=0.01$, $h=1$, $\delta=1$ [Figs. 6(c) and 7(c), homogeneous membrane, $I^{\text{lim}}=2.0$]. This effect is analyzed in the next section.

III. LIMITING “ION-EXCHANGE FUNNEL” MODEL

We wish to analyze the effect described in the previous section, employing the fact that it takes place even for a very thin coating. More precisely, we wish to derive from the full two-layer formulation (3)–(20) a simple limiting model, asymptotically valid for $\varepsilon \rightarrow 0$, $N \rightarrow \infty$, such that their product

$$\stackrel{\text{def}}{\beta} = \varepsilon N = O(1) \quad (25)$$

remains finite. For this purpose we first rewrite Eqs. (5),(6) in a more convenient form in terms of total charge carriers concentration σ , defined as

$$\stackrel{\text{def}}{\sigma} = p + n. \quad (26)$$

Substitution of Eq. (26) into the sum of Eqs. (5) and (6) yields, using Eqs. (6), (7), and (20),

$$\nabla \left(\nabla \sigma + N \frac{\nabla \sigma}{\sigma - N} \right) = 0, \quad \delta < x < \delta + \varepsilon, \quad 0 < y < 1, \quad (27)$$

whereas the continuity conditions (8),(9) and (10),(11) yield, respectively,

$$\left(\sigma_x + N \frac{\sigma_x}{\sigma - N} \right) \Big|_{x=\delta+0} = 2c_x \Big|_{x=\delta-0}, \quad (28)$$

$$[\sigma^2(\delta+0,y) - N^2] = 4c^2(\delta-0,y). \quad (29)$$

On the other hand, substitution of Eq. (26) into the sum of boundary conditions (12) and (13) yields, using Eqs. (7) and (20),

$$\left(\sigma_x + N \frac{\sigma_x}{\sigma - N} \right) \Big|_{x=\delta+\varepsilon} = \begin{cases} -i, & 0 < y < h, \\ 0, & h < y < 1. \end{cases} \quad (30)$$

Integration of Eq. (27) with respect to x over the interval $\delta < x < \delta + \varepsilon$ yields, to the leading order in ε , using Eqs. (28)–(30)

$$\beta v_{yy} - 2c_x \Big|_{x=\delta} = \begin{cases} i, & 0 < y < h, \\ 0, & h < y < 1. \end{cases} \quad (31)$$

Here, β is defined by Eq. (25) and

$$v(y) = \frac{\sigma(\delta,y)}{N} - 1 + \ln \left(\frac{\sigma(\delta,y)}{N} - 1 \right). \quad (32)$$

Eqs. (29),(32) yield

$$v(y) = \sqrt{1 + \frac{4}{N^2} c^2(\delta,y) - 1} + \ln \left(\sqrt{1 + \frac{4}{N^2} c^2(\delta,y) - 1} - 1 \right) = \ln \frac{2}{N^2} + 2 \ln c(\delta,y) + \frac{2}{N^2} c^2(\delta,y) + o \left(\frac{1}{N^2} \right).$$

Equation (31) is obtained using the relations

$$\int_{\delta}^{\delta+\varepsilon} w(x,y) dx = \varepsilon v(y) + O(\varepsilon^2),$$

where

$$w = \frac{\sigma(x,y)}{N} - 1 + \ln \left(\frac{\sigma(x,y)}{N} - 1 \right).$$

Thus,

$$\begin{aligned} v_{yy} &= 2 \left(\frac{c_y(\delta,y)}{c(\delta,y)} \right)_y + \frac{4}{N^2} [c(\delta,y) c_y(\delta,y)]_y \\ &= 2 \left(\frac{c_y(\delta,y)}{c(\delta,y)} \right)_y + O \left(\frac{1}{N^2} \right). \end{aligned} \quad (33)$$

Substitution of Eq. (33) into Eq. (31) finally yields

$$\beta \left(\frac{c_y(\delta,y)}{c(\delta,y)} \right)_y - c_x(\delta,y) = \begin{cases} i/2, & 0 < y < h, \\ 0, & h < y < 1. \end{cases} \quad (34)$$

Boundary condition (34) together with the Laplace equation (3) for $c(x,y)$, the symmetry conditions (14)–(17), and the boundary condition (18) form the limiting asymptotic model of ionic transport in the diffusion layer at a modified heterogeneous membrane. In this model, the entire ionic transport in the coating is reduced to a single nonlinear boundary condition (34). For convenience we reproduce below the respective BVP, which reads

$$0 < x < \delta, \quad 0 < y < 1, \quad \Delta c = 0, \quad (35)$$

$$x = 0, \quad 0 < y < 1, \quad c(0,y) = 1, \quad (36)$$

$$x = \delta, \quad 0 < y < 1, \quad \beta \left(\frac{c_y(\delta,y)}{c(\delta,y)} \right)_y - c_x(\delta,y) = \begin{cases} i/2, & 0 < y < h, \\ 0, & h < y < 1, \end{cases} \quad (37)$$

$$0 < x < \delta, \quad y = 0, 1, \quad c_y \Big|_{y=0,1} = 0. \quad (38)$$

The BVP (35)–(38) was rigorously analyzed in Ref. [4] and was shown to be well posed, that is to possess a unique classical solution. Moreover, it was shown that for any finite value of the “funneling” parameter β , the value of the limiting current in the system is $2/\delta$, that is, the one for a homogeneous membrane. This result is easily recovered by inspection. Indeed, the limiting current is that current value for which the lowest interface concentration at $x = \delta, y = 0$ vanishes. On the other hand, by inspection, the flat one-dimensional concentration distribution,

$$c(x,y) = 1 - \frac{x}{\delta}, \quad (39)$$

with an identically vanishing interface concentration at $x = \delta$ is a solution to Eqs. (35)–(38) (unique by Ref. [4]) cor-

responding to the limiting current $I^{\text{lim}} = i^{\text{lim}} h = 2/\delta$. Given this result for any finite β , the natural question to be addressed is how does, for a vanishing β , the limiting current acquire its low “heterogeneous” value. The answer to this question is provided by the following asymptotic reasoning valid for $\beta \rightarrow 0$ and based too upon the analysis of Ref. [4]. Let I_h^{lim} be the limiting current at the unmodified heterogeneous membrane. For $\beta \rightarrow 0$ and $I \leq I_h^{\text{lim}}$, the concentration distribution at a modified membrane is identical to that at an unmodified one. For $\beta \rightarrow 0$ and $I > I_h^{\text{lim}}$, the interface $x = \delta$ is split, by some point $y_0(I)$, into the following two parts. To the left of $y_0(I)$ the interface concentration essentially vanishes whereas, to the right of $y_0(I)$, the surface modification is not sensed. The position of the “interface free boundary” $y_0(I)$ is determined from the current conservation in the system. The BVP (35)–(38) is asymptotically reduced to that for an unmodified heterogeneous membrane for $I \leq I_h^{\text{lim}}$ and to the following interface free boundary problem for $I > I_h^{\text{lim}}$:

$$0 < x < \delta, \quad 0 < y < 1, \quad \Delta c = 0, \quad (40)$$

$$x=0, \quad 0 < y < 1, \quad c(0,y)=1, \quad (41)$$

$$x=\delta, \quad 0 < y < y_0(I), \quad c(\delta,y)=0, \quad (42)$$

$$x=\delta, \quad y_0(I) < y < 1, \quad c_x(\delta,y) = - \begin{cases} i/2, & 0 < y < h, \\ 0, & h < y < 1, \end{cases} \quad (43)$$

$$0 < x < \delta, \quad y=0,1, \quad c_y|_{y=0,1}=0, \quad (44)$$

$$\int_0^1 c(\delta,y) dy = 1 - \frac{I\delta}{2} \stackrel{\text{def}}{=} (I=ih). \quad (45)$$

Here Eq. (45) is the current conservation condition obtained by integration of Eq. (40) over the range $0 < y < 1$, taking into account Eqs. (38), and integrating the resulting equation twice over the range $0 < x < \delta$, taking into account Eqs. (36), (37). Equation (45) is employed for determination of $y_0(I)$. With I increasing in the range $I_h^{\text{lim}} < I < 2/\delta$, $y_0(I)$ monotonically increases, until reaches 1 for $I = 2/\delta$ (limiting current through a homogeneous membrane).

The interface free boundary problem (40),(45) represents the leading order outer limiting problem of the boundary singular perturbation problem (35)–(38). In order to be able to recover the full voltage/current curve (and not only the value of the limiting current and the concentration wherever it is not too low) one has to consider the respective inner problem, namely, the one determining the low interface concentration $\underline{c}(\delta,y) = o(1)$ in the interval $0 < y < y_0(I)$, approximated in the outer problem by a sheer zero. When this low inner concentration $\underline{c}(\delta,y)$ is found, the voltage V in the system may be identified, in accordance with Eq. (20) as $\ln \underline{c}(\delta,0)$. The inner interface concentration $\underline{c}(\delta,y)$ is found from the free boundary condition (37), rewritten as

$$\beta [\ln \underline{c}(\delta,y)]_{,yy} - c_x(\delta,y) = \begin{cases} i/2, & 0 < y < h, \\ 0, & h < y < 1. \end{cases} \quad (46)$$

Here $\beta \ln \underline{c} = O(1)$ [$\ln \underline{c} = O(1/\beta)$] and $c_x(\delta,y) = O(1)$ is taken from the solution of the outer problem (40)–(45).

As a convenient first approximation (see the Appendix) one may use for $c_x(\delta,y)$ the expression

$$c_x(\delta,y) = -\frac{1}{\delta}. \quad (47)$$

Substitution of Eq. (47) into (46) yields for $\underline{c}(\delta,y)$ a simple differential equation

$$\beta u_{,yy} = \alpha(i,y), \quad (48)$$

where

$$u(y) = \underline{c}(\delta,y), \quad (49)$$

$$\alpha = -\frac{1}{\delta} + \begin{cases} i/2, & 0 < y < h, \\ 0, & h < y < 1. \end{cases} \quad (50)$$

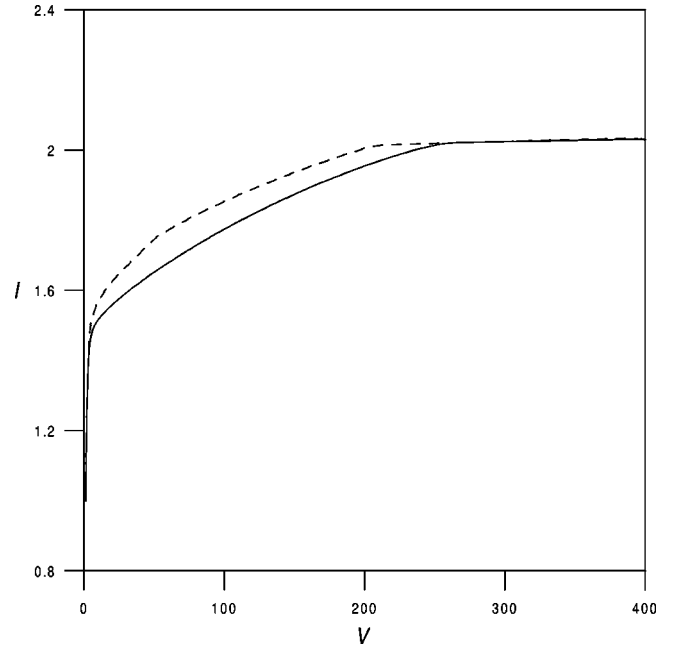


FIG. 8. Calculated VC curves of a modified membrane. — — —, two-layer model ($\varepsilon=0.1$, $N=0.01$, $h=0.5$, $\delta=1$); —, limiting “funnel” model ($\beta=0.001$, $h=0.5$, $\delta=1$).

Explicit integration of Eq. (48), with boundary conditions

$$u_y(0) = 0, \quad (51)$$

$$u(y_0) = 0, \quad (52)$$

following, respectively, from the first of symmetry conditions (44) and the equality $\ln \underline{c}(\delta,y_0) = O(1/\beta)$, yields $u = u(y,i,\beta)$. This, in turn, yields an analytic expression for the voltage/current curve, given by the relation

$$V = -u(0,i,\beta). \quad (53)$$

(See the Appendix for an explicit formula.) In Fig. 8 we compare a VC curve recovered from a numerical solution of the full two-layer formulation (3)–(20) with that obtained from a much simpler, but still numerical, solution of the limiting “funnel” problem (40)–(45). (For the respective 2D concentration distributions see Figs. 7 and 9.) In Fig. 10 we compare this latter VC curve with that obtained from an approximate analytic solution of the interface free boundary problem (40)–(53).

IV. DISCUSSION: PHYSICAL MECHANISM OF ION-EXCHANGE FUNNELING

Our message in this paper to a general physical audience interested in interface transport is not, of course, the possi-

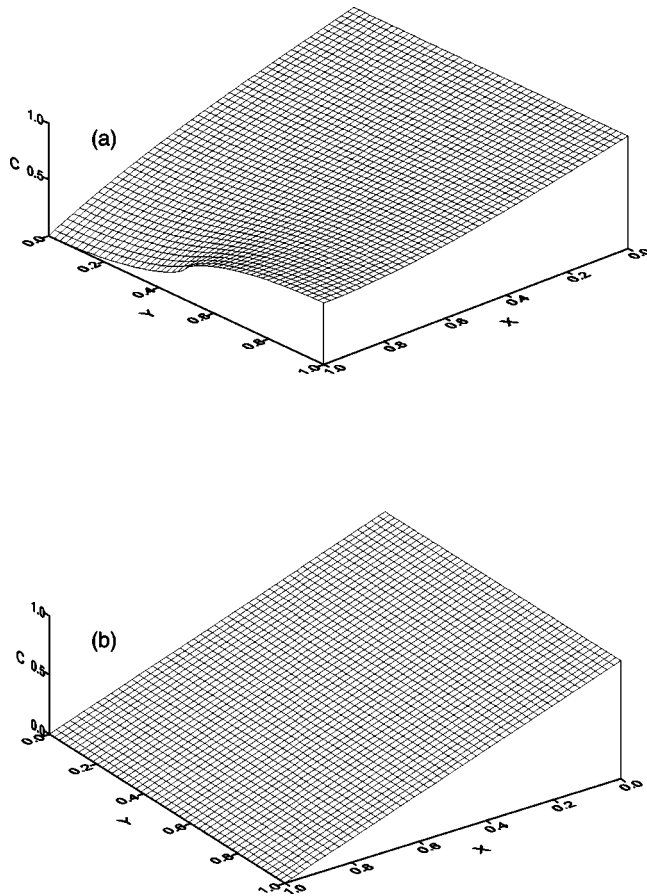


FIG. 9. 2D concentration distribution in the limiting (funnel) model. (a) $\beta=0$, $h=0.5$, $\delta=1$, $I=I^{\text{lim}}=1.46$; (b) $\beta=0.001$, $h=0.5$, $\delta=1$, $I=I^{\text{lim}}=I_h^{\text{lim}}=2$.

bility to reduce concentration polarization at a heterogeneous membrane by a polyelectrolyte coating of the latter. Such a message would be more appropriate for a membranological journal. The message is that a very classical kinematic problem of two-dimensional steady state electrodiffusion onto a nonuniform surface from a region with a peculiar geometry may be reduced, through a suitable asymptotic treatment, to an even more classical simple diffusion problem in a region with a trivial geometry. In this latter problem all peculiarities of the original problem are concentrated in a single, apparently very simple, singularly perturbed nonlinear boundary condition (37). Singularity lies in the fact that an arbitrarily small perturbation of this kind yields, through a particular nonlinear mechanism, a large effect upon the ionic transport in terms of the limiting current—a situation reminiscent of the viscous drag resolution of the D’Alambert paradox in the high Reynolds number potential flow around a symmetric body. Having said this, let us recapitulate the major facts referred to above and throughout this paper and close with a semantic comment.

The ac or infinitesimal dc current resistance of a heterogeneous electro dialysis membrane is determined by percolation of the ion-exchange beads in it’s bulk. At the same time, the finite dc current resistance of a heterogeneous membrane is dominated by concentration polarization. This latter is de-

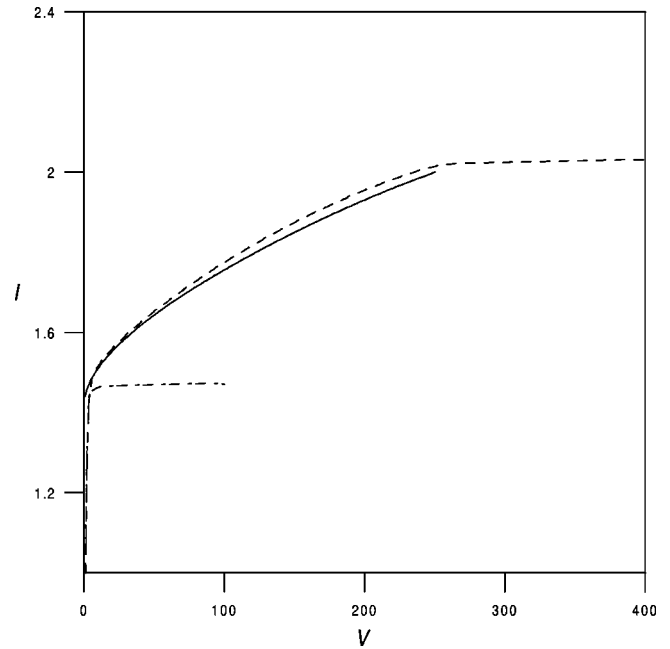


FIG. 10. Calculated VC curves in the limiting (funnel) model. ---, $\beta=0.001$, $h=0.5$, $\delta=1$; - · -, $\beta=0$, $h=0.5$, $\delta=1$; —, approximate formula (A7).

termined by the geometry of alternating ion conductive and insulating regions at the membrane’s surface in relation to the width of the depleted diffusion layer of the surrounding electrolyte. The major quantitative characteristic of this dc concentration polarizability of a heterogeneous membrane is the value of the limiting current through it compared to that through a homogeneous membrane. Remarkably, a very thin coating of a heterogeneous membrane by a slightly charged

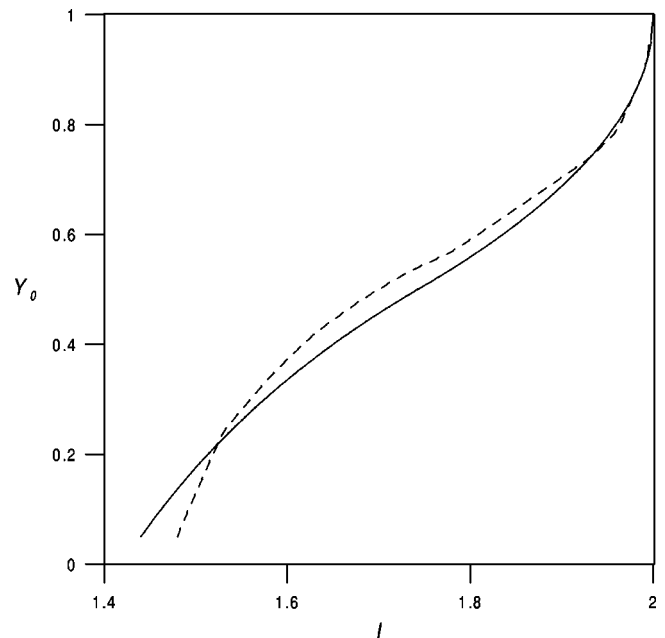


FIG. 11. $y_0(I)$ plot. ---, numerical solution; —, approximate formula (A6).

homogeneous ion-exchange layer brings the limiting current to a value typical of a homogeneous membrane. In this paper we termed this effect “ion-exchange funneling.” We wish to comment now on this term.

The lateral counter-ion flux along the membrane surface from the insulating to the conductive part of it is $j_+ = -p_y - p\varphi_y$ (or, respectively, $j_+ = -c_y - c\varphi_y$ for the solution layer adjacent to a heterogeneous membrane).

Why is the counterion transport in the coating so much more effective than that in the solution layer of a similar thickness? Let us point out first that, by Eqs. (20),(29), the counter-ion gradient in the coating, the concentration gradient near the interface, and the electric potential gradient therein are of the same order of magnitude:

$$|p_y| \sim |c_y| \sim |\varphi_y|.$$

On the other hand, for $\varepsilon \rightarrow 0$, $N \rightarrow \infty$, so that $\beta = \varepsilon N = \text{const} = O(1)$, the migrational counterion flux component in the coating will be N times larger than any other flux component (either diffusional one in the coating or diffusional and electromigrational one in a solution layer near an unmodified heterogeneous membrane). Thus, a lateral concentration drop from the insulating to a conductive part of a heterogeneous membrane surface produces a respective lateral electric potential drop which, in turn, yields a major electromigrational counterion flow towards the “ionic gates” to the membrane. This is reminiscent of a funnel conducting the liquid collected at its surface to the orifice: the analogy that suggested the term “ion-exchange funneling.”

ACKNOWLEDGMENT

We are grateful to Professor Ora Kedem for introducing us to the modified heterogeneous membranes problem.

APPENDIX: APPROXIMATE SOLUTION OF THE LIMITING (FUNNEL) PROBLEM FOR SMALL VALUES OF FUNNELING PARAMETER

Below we outline the construction of an approximate solution to the limiting problem (35)–(38), and of the respective voltage/current curve, valid for small values of the funneling parameter β . We start with an approximate solution to the mixed limiting BVP (40)–(44) (with a fixed y_0) provided by the first approximation of the Schwarz alternating procedure [5]. For this purpose, the Laplace equation (40) is first solved in the “full” domain $0 < x < \delta$, $0 < y < 1$ with boundary conditions (41),(43),(44) and condition (42) applied on the entire interface $x = \delta$, $0 < y < 1$. This yields the one-dimensional “flat” concentration distribution (39). Next, Eq. (40) is solved by separation of variables in the “right” sub-region $0 < x < \delta$, $y_0 < y < 1$ with boundary conditions (41), (43) and [see Eqs. (39),(44)]

$$c_y^{(2)}(x,1) = 0, \quad (\text{A1})$$

$$c^{(2)}(x,y_0) = 1 - \frac{x}{\delta}. \quad (\text{A2})$$

The solution reads

$$c^{(2)}(x,y) = \begin{cases} 1 - \frac{x}{\delta} + \sum_{n=1,3,5,\dots} \frac{8(1-y_0)}{\pi^2 n^2 \delta} \frac{1}{\cosh\{\delta\pi n/[2(1-y_0)]\}} \sin\left(\frac{\pi n[y-y_0]}{2(1-y_0)}\right) \sinh\left(\frac{\pi n x}{2(1-y_0)}\right) \\ \text{for } I \text{ such that } y_0(I) \geq h, \\ \\ 1 - \frac{x}{\delta} + \sum_{n=1,3,5,\dots} \frac{8(1-y_0)}{\pi^2 n^2} \left[\frac{1}{\delta} - \frac{i}{2} \left(1 - \cos \frac{\pi n(h-y_0)}{2(1-y_0)} \right) \right] \frac{1}{\cosh\{\delta\pi n/[2(1-y_0)]\}} \sin\left(\frac{\pi n[y-y_0]}{2(1-y_0)}\right) \sinh\left(\frac{\pi n x}{2(1-y_0)}\right) \\ \text{for } I \text{ such that } y_0(I) \in (0,h). \end{cases} \quad (\text{A3})$$

Substituting $x = \delta$ into Eq. (A3) we find

$$c^{(2)}(\delta,y) = \begin{cases} \sum_{n=1,3,5,\dots} \frac{8(1-y_0)}{\pi^2 n^2 \delta} \tanh\left(\frac{\pi n \delta}{2(1-y_0)}\right) \sin\left(\frac{\pi n[y-y_0]}{2(1-y_0)}\right) & \text{for } I \text{ such that } y_0(I) \geq h, \\ \\ \sum_{n=1,3,5,\dots} \frac{8(1-y_0)}{\pi^2 n^2} \left[\frac{1}{\delta} - \frac{i}{2} \left(1 - \cos \frac{\pi n(h-y_0)}{2(1-y_0)} \right) \right] \tanh\left(\frac{\pi n \delta}{2(1-y_0)}\right) \sin\left(\frac{\pi n[y-y_0]}{2(1-y_0)}\right) & \text{for } I \text{ such that } y_0(I) \in (0,h). \end{cases} \quad (\text{A4})$$

Substitution of Eq. (A4) into Eq. (45) yields

$$\sum_{n=1,3,5,\dots} \frac{16(1-y_0)^2}{\pi^3 n^3 \delta} \tanh \frac{\pi n \delta}{2(1-y_0)} = 1 - \frac{I\delta}{2} \quad \text{for } I \text{ such that } y_0(I) \geq h,$$

$$\sum_{n=1,3,5,\dots} \frac{16(1-y_0)^2}{\pi^3 n^3} \left[\frac{1}{\delta} - \frac{i}{2} \left(1 - \cos \frac{\pi n (h-y_0)}{2(1-y_0)} \right) \right] \tanh \left(\frac{\pi n \delta}{2(1-y_0)} \right) = 1 - \frac{I\delta}{2} \quad \text{for } I \text{ such that } y_0(I) \in (0, h). \quad (\text{A5})$$

Equation (A5) yields $y_0(I)$ in the form

$$y_0(I) \approx \begin{cases} 1 - \frac{\pi}{4} \sqrt{\pi \delta \left(1 - \frac{I\delta}{2} \right)} & \text{for } I \geq I^1 \stackrel{=}{\text{def}} \frac{2}{\delta} \left[1 - \frac{16}{\pi^3} (1-h)^2 \right] \\ 1 - \left[\frac{I}{\pi} \frac{h-1}{h} - \sqrt{\frac{I^2}{\pi^2} \left(\frac{h-1}{h} \right)^2 - \left(\frac{I\delta}{2} - 1 - \frac{I}{\pi h} (h-1)^2 \right) \left(\frac{16}{\pi^3 \delta} - \frac{I}{\pi h} \right)^2} \right] & \\ \left(\frac{16}{\pi^3 \delta} - \frac{I}{\pi h} \right) & \text{for } I_0^{\text{lim}} \leq I \leq I^1. \end{cases} \quad (\text{A6})$$

In Fig. 11, thus calculated $y_0(I)$ is compared with that found numerically from a numerical solution of the interface free boundary problem (40)–(45). The construction of approximate voltage/current curve is completed by employing the calculated $y_0(I)$ in solution of BVP (48)–(52), yielding, in accordance with Eq. (53),

$$V \approx \frac{1}{2\beta} \begin{cases} \left(\frac{I}{h} - \frac{2}{\delta} \right) \left(h y_0(I) - \frac{h^2}{2} \right) - \frac{1}{\delta} (y_0 - h)^2 & \text{for } I \geq I^1, \\ \frac{y_0^2(I)}{2} \left(\frac{I}{h} - \frac{2}{\delta} \right) & \text{for } I_0^{\text{lim}} \leq I \leq I^1. \end{cases} \quad (\text{A7})$$

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