Overlimiting current due to electro-diffusive amplification of the second Wien effect at a cation-anion bipolar membrane junction

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Numerical simulations are presented for the transient and steady-state response of a model electrodiffusive cell with a bipolar ion-selective membrane under electric current. The model uses a continuum Poisson-Nernst-Planck theory including source terms to account for the catalytic second Wien effect between ionogenic groups in the membranes and resolves the Debye layers at interfaces. The resulting electric field at the membrane junction is increased by as much as four orders of magnitude in comparison to the field external to the membrane. This leads to a significant amplification of the second Wien effect, creating an increased ionic flux due to the catalytic decomposition of water. The effect also induces an exaltation effect wherein the salt ion flux undergoes a concomitant increase as well. The interplay of effects results in a unique over-limiting current mechanism due to concentration polarization internal, rather than external, to the membranes. In addition to the case of two equal but oppositely charged membranes under the standard simplifying assumption of equal ionic diffusivities, two variations on this model are studied. Asymmetric diffusivities, representative of the actual mobility difference in dissociated water ions, and the effect of the membrane charge density ratio were also considered. The latter elucidates an overlimiting current shift mechanism for DNA adsorption on anion-selective membranes proposed by Slouka *et al.* [Langmuir **29**, 8275 (2013)]. The former provides more realistic picture of multi-ion transport and demonstrates a surprising steady-state effect due to the asymmetry in the diffusivity of hydroxide and hydronium. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5066195>

I. INTRODUCTION

Cation-anion selective, i.e., bipolar, membrane junctions are being employed as ion-fluidic transistors¹ and photoelectrochemically active elements,² as well as in industry as part of membrane electrodialysis systems for the production of acids and alkalis from salt solutions, for desalination³ and correcting the pH of solutions,^{4,5} for the separation of carbon dioxide from air,⁶ and for the case when water is deionized by the method of continuous deionization.⁷ Bipolar membranes also find use in soil and water restoration for the separation of heavy metals.⁸

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While the electro-diffusive transport governing the distribution of ions and potential is essentially similar in bipolar and monopolar membranes, the details of how concentration polarization (CP) develops and how it affects the current-voltage characteristic are somewhat different in the two cases. Thus, it is worth reviewing the canonical picture of current-voltage response in the monopolar ion-selective system before discussing the contrasting case of bipolar membranes. At low voltage, the response appears Ohmic as CP develops across the system resulting in depletion and enrichment of ions at opposite interfaces. At a sufficiently high current density, the classical limiting current,⁹ the concentration approaches zero at the depleted interface. However, at such low local ionic strength, local electroneutrality cannot be maintained, and a distinct nonequilibrium extended space charge (ESC) develops.¹⁰ This transition can be correlated with a decrease in the current-voltage slope, corresponding to the increased resistance of the system due to depletion and subsequent ESC development. At higher voltages, there is typically another distinct transition to an over-limiting current (OLC) which may be caused by one or more mechanisms that have been the subject of many studies.^{11–21} The dominant OLC mechanism for a given system was shown by Dydek *et al.*²² to be determined essentially by the Bikerman number. Critically, for monopolar interfaces, all these mechanisms depend on the development of CP in the electrolyte layers external to the membrane, where the fixed charge density is low, i.e., on the membrane exterior or, if any, microchannel walls. This turns out not to be the case at all for the bipolar membranes, where the external CP is suppressed, and the effects are instead driven by high fields produced by interior concentration gradients. While overlimiting current (OLC) has been observed in bipolar membranes and enhanced water-dissociation has been suspected as contributing,²³ theoretical studies of the role of ion concentration polarization in catalytic decomposition of water are lacking.

In addition to the typical fabricated bipolar membranes,²⁴ another important example of a bipolar membrane junction effect occurs when negatively charged DNA adsorbs to the surface of an anion-exchange membrane, such as in the membrane sensor of Slouka *et al.*²⁵ The OLC transition voltage, observed as a characteristic inflection in the voltage-current characteristic, shifts with increasing DNA concentration in solution. At intermediate and high DNA concentration, corresponding to high surface coverage, hence higher charge density, both the transition voltage and the slope in the OLC region increase with increasing DNA concentration. The very low DNA concentration regime likely involves complex interplay of electrohydrodynamics and DNA conformation, but the intermediate-to-high concentration regime may be studied and understood purely in terms of electrodiffusive-reactive ion transport. Thus, any conclusions that can be drawn from the present study will be applicable to the regime of high DNA surface coverage.

The first theoretical treatment of a bipolar membrane junction relied on the phenomenological and mathematical similarity between electrodiffusive drift at the $p-n$ junction in semiconductors and electrodiffusive ion-selective transport through membranes.^{10,26} Water dissociation at the membrane interface was investigated by Greben, Pivovarov, and Kovarsky,²⁷ Simons,²⁸ Timashev and Kirganova,²⁹ Mafe, Ramirez, and Alkaraz,³⁰ Zabolotsky, Gnusin, and Sheldeshov,³¹ in which the high dissociation rate was explained by both the catalytic mechanism and the second Wien effect. These studies relied on the Debye-Huckel approximation. However, Conroy *et al.*³² relaxed this assumption, using the full Nernst-Planck-Poisson-Stokes system along with water recombination and dissociation. In general, additional dissociation of hydrogen cations and hydroxyl anions near the junction contributes to the total electric current passing through the system and can contribute to the overlimiting current.³⁰

In these previous studies, only the processes inside the porous membranes were considered. Ion concentration polarization (ICP) in the exterior boundary layers plays a crucial role in many of the usual overlimiting current (OLC) mechanisms,^{17,22,33} including time-dependent modulation of the effective transport number.³⁴ Therefore, we present a theoretical study of the electrodiffusive transport of both electrolyte and dissociated water ions in a cell with a bipolar membrane and two adjacent bulk electrolyte layers under constant applied electric field. The dissociation of water molecules through the second Wien effect as well as through chemical reactions with functional groups in the membranes is taken into account via nonlinear source terms. By including ion transport in the electrolyte layers as well as the membrane junction, we demonstrate that the water dissociation is enhanced by an internal concentration polarization which falls largely across the two

membranes and suppresses external ICP. This demonstrates an OLC mechanism at a bipolar membrane junction that is quite distinct from other OLC mechanisms at monopolar membranes. Here, overlimiting currents occur in the absence of large, external concentration gradients. This should be observable in experiments. In addition to considering the basic mechanism, we also present a comparison of the effect taking into account the often-ignored disparity in ion diffusivity and examine the effect of varying the charge density in one membrane. We then discuss some implications of these results.

II. THEORY

The system is modeled using a three-layer “electrolyte-bipolar membrane-electrolyte” configuration (see Fig. 1). The electrolyte is assumed to be strong, i.e., completely dissociated in solution. Along with the transport of salt ions in the electrolyte and non-ideal membranes, dissociation of water into ions and subsequent transport is included. An external electric field is directed normal to the membrane, and the resulting current density is assumed to be sufficiently below the range wherein current-induced dehydration can occur at the membrane junction.³⁵ In each of the regions, electro-diffusion and reactions are governed by the dimensionless Nernst-Planck-Poisson equations, including a source term for hydrogen and hydroxyl,

$$\frac{\partial c^\pm}{\partial t} = \pm \nabla \cdot (c^\pm \nabla \Phi) + \nabla^2 c^\pm, \quad (1)$$

$$\frac{\partial c_a^\pm}{\partial t} = D_a^\pm \nabla \cdot [\pm (c_a^\pm \nabla \Phi) + \nabla c_a^\pm] + F^\pm, \quad (2)$$

with respect to the concentration of the salt ions $c^\pm$ (for example, K^+ and Cl^-) and water ions $c_a^\pm$ (H^+ and OH^-). Here, we keep the usual assumption of a symmetric, binary salt. But given that the mobilities of hydroxide and hydroxyl differ by a significant amount,³⁶ we consider both the case where $D_a^\pm = 1$ and the case where $D_a^+ = 4.59$ and $D_a^- = 2.6$, i.e., representative of the actual physical situation. The equations for the water ions include source terms $F^\pm$ associated with the chemical reactions of dissociation and recombination of water ions, which will be discussed subsequently. The electric potential Φ obeys the Poisson equation,

$$\nu^2 \nabla^2 \Phi = (c^- - c^+) + (c_a^- - c_a^+) + N, \quad (3)$$

where the term on the right hand side corresponds to the charge density. This includes the term N , which is the fixed volume charge density, defined piecewise in each of the membrane regions: $N = 0$ for regions I and IV outside of the porous membrane; $N = N_1 = \text{const} > 0$ for the cation-exchange

FIG. 1. Schematic geometry of the bipolar membrane showing boundary conditions and geometry.

membrane II and $N = N_2 = \text{const} < 0$ for the anion-exchange membrane III, see Fig. 1. A similar approach, when the systems in the electrolyte and membrane regions differ only by the source term N , was used in the study of non-ideal mono- and bipolar membranes.^{32,37} With this approach, fully resolving the electric double-layers at boundaries, it is not necessary to set boundary conditions on the membrane surface and is possible to solve the three-layer system as one with a piecewise constant function N . Reservoir boundary conditions at $y = -L$ and $y = L + 1$ complete the problem:

$$y = -L: \quad c^\pm = 1; \quad c_a^\pm = c_a, \quad \Phi = 0, \quad (4)$$

$$y = L + 1: \quad c^\pm = 1, \quad c_a^\pm = c_a, \quad \Phi = \Delta V. \quad (5)$$

System (1)–(5) is presented above in dimensionless form, with the same standard scalings used for monopolar membrane problems (see, for example, Ref. 16). Elsewhere in the paper, variables with tilde are used for the dimensional variables, as opposed to their dimensionless counterparts without tilde.

There are several possible approaches to the source terms, $F^\pm$. In the simplest case, the chemical reaction of water dissociation is taken into account both in the electrolyte and in the membrane,

where $\tilde{k}_d = 2.7 \times 10^{-5} \text{ s}^{-1}$ and $\tilde{k}_r = 1.5 \times 10^8 \text{ m}^3/\text{mol s}$ are the rates of dissociation and recombination of water molecules, respectively.³⁸ In this case, the source terms become

$$F^\pm = k_d - k_r c_a^+ c_a^-. \quad (7)$$

The theory predicts a low rate of water dissociation for such a case, and it was shown in Ref. 29 that the coefficient k_d is, in fact, a function of the electric field, namely, $k_d = k_d(0) \exp(\beta|E|)$ with $\beta = \tilde{a}/\tilde{h}$. Here, $\tilde{h}$ is the characteristic scale of the problem, and $\tilde{a}$ is an empirical parameter, which in Ref. 32 was assumed to be equal to $\tilde{a} = 1.38 \times 10^{-8} \text{ m}$.³⁹ This dependence of the dissociation constant on electric field is called the second Wien effect. As Danielsson noted,³⁸ the explanation of the enhanced dissociation of water by the second Wien effect alone has several significant drawbacks. The main drawback is that the second Wien effect predicts the same dissociation in both cation- and anion-exchange membranes, which does not correspond to the experimental data. Simons⁴⁰ suggested and improved the theory of water dissociation based upon the inclusion of chemical reactions between the membrane ionogenic groups and water. The key idea is that the dissociation of water is accelerated by some organic bases B and acids AH contained in membranes. So, for the anion-exchange membranes,

and for the cation-exchange membranes,

The direct rate constants can be calculated from the equilibrium constants and the reverse rate constants using the relation provided by Simons.⁴⁰ The reaction rates depend upon the type of

membrane, specifically the group(s) present. The limiting reaction for the basic groups BH is the direct reaction (9), and for acidic groups AH is the direct reaction (11). The phosphonic ionogenic groups in bipolar membranes are responsible for a particularly strong effect on the catalytic dissociation of water, with the rate of the limiting reaction between $10 - 10^3 \text{ s}^{-1}$.⁴¹ This effect exceeds that of sulphonic groups with $\tilde{k}_L = 3 \times 10^{-3} \text{ s}^{-1}$, primary and secondary amino groups with $\tilde{k}_L = 10^{-1} \text{ s}^{-1}$, tertiary amino groups with $\tilde{k}_L = 10^0 \text{ s}^{-1}$, and even carboxyl groups with $\tilde{k}_L = 10^1 \text{ s}^{-1}$.

Including both the second Wien effect and the catalytic reaction with ionogenic groups, the source terms take the following form:

$$F_{\text{II}}^+ = \left(k_3 \alpha \frac{k_4 \alpha + k_{-3} c_a^+}{k_3 \alpha + k_{-4} c_a^+} - k_{-3} c_a^+ \right) |N| + k_d \alpha - k_r c_a^+ c_a^-, \quad (12)$$

$$F_{\text{III}}^+ = \left(k_2 \alpha - k_{-2} \frac{k_2 \alpha + k_{-1} c_a^-}{k_1 \alpha + k_{-2} c_a^-} c_a^+ \right) |N| + k_d \alpha - k_r c_a^+ c_a^-, \quad (13)$$

$$F_{\text{II}}^- = \left(k_4 \alpha - k_{-4} \frac{k_4 \alpha + k_{-3} c_a^+}{k_3 \alpha + k_{-4} c_a^+} c_a^- \right) |N| + k_d \alpha - k_r c_a^+ c_a^-, \quad (14)$$

$$F_{\text{III}}^- = \left(k_1 \alpha \frac{k_2 \alpha + k_{-1} c_a^-}{k_1 \alpha + k_{-2} c_a^-} - k_{-1} c_a^- \right) |N| + k_d \alpha - k_r c_a^+ c_a^-, \quad (15)$$

where $\alpha = \exp(\beta|E|)$. These relations were derived under the assumptions: $\text{BH}^+ \gg \text{B}$, $\text{OH}^- \gg \text{B}$ for AEM and $\text{A}^- \gg \text{AH}$, $\text{H}_3\text{O}^+ \gg \text{AH}$ for CEM. The source terms $F^\pm$ are piecewise-defined functions, $F^\pm$ given by (7) in regions I and IV, $F^\pm = F_{\text{II}}^\pm$ in region II, and $F^\pm = F_{\text{III}}^\pm$ in region III. Such a formulation was considered in Ref. 42. The reaction rates k_i and k_{-i} are constants and are the parameters of the problem.

III. RESULTS

Numerical integration of the one-dimensional non-stationary problem (1)–(5) was carried out using the semi-implicit Runge-Kutta method in time and a finite difference scheme in space. Details of this method can be found in Ref. 16. Overall, electroneutrality was chosen as the initial condition. Two junctions with different charge density distributions were considered. For case 1, the membranes in regions II and III were taken as antisymmetric, with $N_1 = 10$, and $N_2 = -10$. Therefore, the coefficients of the rates of chemical reactions were also taken to be equal, $k_1 = k_3 = 10$, $k_2 = k_4 = 0.1$, $k_{-1} = k_{-3} = 3 \times 10^8$, and $k_{-2} = k_{-4} = 10^8$. In case 2, the charge density N_1 is reduced to $N_1 = 5$ while $N_2 = -10$, so the reaction rates in region II, k_3 , k_{-3} , k_4 , and k_{-4} , are halved. The usual simplifying assumption of equal ionic diffusivities is indicated by primes; the unprimed cases have unequal mobilities for the dissociated water ions. The values of the charge density are somewhat low for typical ion-exchange membranes, corresponding more closely to that of fabricated glass nanochannels.⁴³ While the overall conductivity and values of the reaction rates depend on the values of the charge density, the main qualitative features and the corresponding underlying mechanisms do not. Similarly, the dimensionless Debye length was taken as $\nu = 10^{-3}$ as a representative value. But as will be discussed subsequently, this has a limited effect on the catalytic decomposition.

The voltage current characteristics for case 1' as $t \rightarrow \infty$ are shown in Fig. 2 both with and without contributions from the second Wien effect. The total electric current through the system, $j = j_c + j_a$, is shown along with that due to the salt ions j_c and that due to the current of the dissociated water ions j_a . In the absence of the second Wien effect, i.e., by taking $\beta = 0$, the current-voltage characteristic exhibits two modes: it obeys the ohmic or underlimiting regime for small ΔV and the limiting regime for moderate ΔV . Including the second Wien effect with $\beta = 10^{-4}$, the overlimiting regime appears as a third mode for sufficiently large ΔV . It is worth noting that this is not solely due

FIG. 2. Steady-state voltage current characteristic and components for case 1' without (solid line) and with (dashed line) the second Wien effect. (a) The total electric current, (b) the salt-ion current, and (c) the current due to dissociated water ions. (d) indicates the behavior of the steady-state current at $\Delta V = 10$ as a function of charge density with (dashed) and without (solid) the second Wien effect.

to the increase in ions from water dissociation, but also there is a concurrent increase in the salt flux. This effect is known alternately as either the exaltation effect or the Kharkats effect.⁴⁴ Increasing the overall charge density decreases the overall current, as the membranes essentially approach the ideal membrane condition and exclude most of the mobile counter-ions. As can be seen in Fig. 2(d), the second Wien effect has a slightly higher current density due to dissociation.

The basic mechanisms for both the exaltation effect and the origin of the excess current are apparent in Fig. 3, showing the $t \rightarrow \infty$ concentration profile of the salt anions (a) and dissociated water anions (b). By virtue of antisymmetry relative to the bipolar membrane junction, the concentrations of the cations can be readily obtained. In this sense, it can be said that the behavior of cations in CEM coincides with the behavior of anions in AEM and vice versa. Several observations can be made. Overall, the degree of concentration polarization exterior to bipolar membranes is considerably lower than in monopolar membranes. Severe depletion of the salt and water ions occurs only at the membrane junction, $y = 0.5$, where electric continuity of electric flux demands a maximum in the electric field intensity (see also Figs. 4 and 5). The field intensity increases dramatically above applied voltages around $\Delta V = 10$ and is practically independent of parameter β in the range of values considered herein (the dependence for $\beta = 0$ and $\beta = 10^{-4}$ in the figure coincides with graphical accuracy). This indicates that the evolution of the electric field is principally driven by the development of interior concentration polarization of the salt ions.

The aforementioned effects are independent of both the second Wien effect and the inclusion of water ions into the picture; the suppression of concentration polarization, which in turn suppresses

FIG. 3. The space distribution of the concentrations of salt ions (a) and water ions (b) for $\Delta V = 20$. The solid line corresponds to calculation without the Wien effect, and the dashed line corresponds to calculation with the Wien effect.

FIG. 4. Dependence of the maximum value of the electric field $|E|$, occurring at the depleted membrane junction, on the potential difference ΔV .

FIG. 5. Hydronium maximum concentration as a function of potential drop ΔV . The solid line corresponds to calculation without the Wien effect, and the dashed line corresponds to calculation with the Wien effect. This maximum concentration also occurs at the junction.

the formation of an extended space charge region, implies that OLC at bipolar membranes cannot be due to non-equilibrium electroconvection⁴⁵ or any other space-charge related effects.³⁷ Field-assisted water dissociation can be expected to saturate at vanishing Debye length. This suggests the principal mode of overlimiting current for bipolar membranes occurs via the second Wien effect amplified by electrodiffusive depletion of the salt ions at the interior membrane junction.

In response to the increased electric field due to depletion near the junction, the concentration of dissociated water ions increases everywhere, but more markedly so in the CEM and flanking concentration polarization layer. As the field strength approaches 10^4 in the depleted junction, the contribution from the second Wien effect begins to overtake the contributions due to non-field dependent source terms, driving the system into a strong overlimiting response, as shown in Figs. 3(b) and 6. Then, as the system attempts to maintain approximate local electroneutrality, the concentration of salt ions [Fig. 3(a)] actually decreases everywhere to the left of the AEM. However, there is an increase in both salt ion and water ion concentration to the right of the CEM-AEM junction. In particular, it is precisely this increase in conductivity at the resistance bottleneck for the system, i.e., near the membrane junction, concurrent with increased concentration polarization across the full bipolar membrane, rather than the change in overall conductivity, which results in the overlimiting current.

The steady-state voltage current characteristics for several different cases are shown in Fig. 6. Some general observations are that the overall electric currents in cases 2 and 2' are higher than cases 1 and 1'. This stems principally from the lower differential resistance of membranes with lower selectivity³⁷ and is consistent from the Ohmic response regime through the overlimiting

FIG. 6. Steady-state voltage current characteristic for the (a) total electric current density, (b) salt ion component, and (c) dissociated water ion component. Primed cases are indicated by dashed lines, unprimed by solid lines.

FIG. 7. Hydronium maximum concentration as a function of potential drop ΔV , comparing all cases.

regime. In particular, the relative changes in differential resistance of the two membranes with voltage due to a variation in membrane selectivity leads to a less saturated current-voltage characteristic in the limiting region for the bipolar junction with $N_1 = -0.5N_2$. However, from Fig. 6(c), it is clear that the second Wien effect does not contribute much to the current density below about $\Delta V = 10$, and that above this, the difference in the dissociation rate is due principally to the fact that the density of catalytic groups is assumed proportional to the membrane charge density. This idea is further supported by the dependence of the maximum hydronium concentration vs applied voltage shown in Fig. 7. Both cases 2 and 2' show a significantly lower maximum concentration at the junction than the respective 1 and 1' cases; yet, at the same time, the voltage current characteristic [see especially Figs. 6(a) and 6(b)] shows an apparent increase even below the amplification of the second Wien effect around $\Delta V = 10$. Furthermore, the difference in maximum field strength (see Fig. 8) and dissociated water current between the 1, 1' and 2, 2' cases would suggest that the onset of the amplified second Wien effect should actually occur at slightly higher voltages in cases 2 and 2'.

As can be seen from the time dynamics in Fig. 6, the current due to salt ions, j_c , reaches a local maximum rather quickly and then decays to a near-steady value by about $t = 7.5$ in all cases. This corresponds with the time required for the concentration profile to develop fully across the membrane, with depletion occurring near the membrane junction. However, the current of water ions, j_a , continues to grow monotonically until it begins to saturate. Note also that j_a for cases 1 and 1' are initially lower and then overtake that for cases 2 and 2'. The time scale for this cross-over is governed by the development of the salt ion concentration profile, i.e., of the depletion-enhanced electric field at the junction. j_a for cases 2 and 2' approach saturation on a time scale governed by the

FIG. 8. Dependence of the maximum value of the electric field $|E|$, occurring at the depleted membrane junction, on the potential difference ΔV comparing cases 1 and 2.

FIG. 9. Corresponding (a) salt cation and (b) water cation concentration profiles; primed cases are shown by dashed lines, unprimed by solid lines.

diffusivity of the dissociated water ions, and the rather flat current compared to cases 1 and 1' is a result of the dissociation reaction being limited by site density of ionogenic groups.

What is interesting is that, even at sufficiently long times to reach an apparent steady-state, the current in the primed cases 1' and 2' with symmetric diffusivities is distinctly different from the unprimed cases. This divergence between the primed and un-primed cases occurs below the rough threshold field maximum (determined essentially by β) where the second Wien effect becomes important. Notice also that the maximum hydronium concentration (see Fig. 7) is already higher below applied voltages of about $\Delta V = 10$ in the primed cases compared to the unprimed cases. Moreover, the maximum electric field strength (Fig. 8) is indistinguishable (to within graphical accuracy) between the primed and un-primed cases, again emphasizing that it is the concentration polarization of the salt ions responsible for field amplification. It is also worth noting that the overall salt concentration tends to be higher and that of the dissociated water ions lower in the un-primed cases compared to the primed cases (see Figs. 9–11), while both the current components due to salt ions and dissociated water ions are lower. Thus, the asymmetry in the diffusivities manifests in the steady-state as a reduction in the exaltation effect.

The divergence between the cases due to the mobility difference is evidently not a unique feature of the second Wien effect, as it occurs below the voltages where the second Wien effect is dominant. However, it does involve the balance of chemical potential and charge neutrality between salt ions, water ions, and fixed charge groups—the same underlying mechanism for the exaltation effect, so it can be associated with the asymmetry in the rates of dissociation and recombination of water. When the contributions from the catalytic second Wien effect become significant, the divergence is even more pronounced.

Interestingly, in addition to the overall reduction in the conductivity underlying the reduced exaltation effect, the asymmetry in the diffusivities also results in a spatial asymmetry in the ion

FIG. 10. Transient response of the (a) salt current and (b) dissociated water ion current for all cases.

FIG. 11. Salt, $K = c^+ + c^-$, and mobile charge, $\rho = c^+ - c^-$, distributions in the steady-state. Note that the case 1' distributions are symmetric about the junction, but the un-primed distributions are asymmetric with a marked increase in asymmetry between cases 2' and 2.

distributions (see Fig. 11) in the steady-state. The underlying reason can be ascertained from the governing equations. For symmetric diffusivities, the current density component due to the dissociated water ions has zero divergence in the steady-state. On the other hand, for asymmetry in the diffusivities of the water ions, the source terms $F^\pm$ give rise to a non-zero divergence in this current-density component. Physically, the asymmetry in the diffusivity implies that stoichiometry for the reactions described by Eqs. (8)–(11) is governed by relative transport rates of the reactants and products. Thus, the steady-state concentrations for the unprimed cases reflect the underlying asymmetry in mobilities through the source terms, with an increase in the overall salt ion concentration and a reduction in the concentrations of dissociated water ions, compared to the primed cases.

IV. CONCLUSIONS

Using a model based on the Nernst-Planck-Poisson system, numerical simulations of the ion transport and distribution through a bipolar membrane under the applied electric field were performed. The dissociation of water was taken into consideration, including reactions with ionogenic groups contained in the membrane. This permitted the influence of the second Wien effect on the magnitude of the electric current to be studied. We have demonstrated that the appearance of an overlimiting current regime coincides with an increase in catalytic water dissociation. The effect is particularly strong near the membrane junction, where electrodiffusive depletion of both salt and dissociated water ions results in amplification of the local electric field. It was further shown that the exaltation effect coincides with a slight increase in salt ion concentration polarization, also driven by the electrodiffusive amplification of the second Wien effect.

Beyond improved understanding of the conventional bipolar membrane systems, two applications of the present work are the study of bipolar “mosaic” membranes⁴⁶ and providing a starting

point for a more detailed study of the role of the second Wien effect on the observed shift in OLC threshold due to DNA adsorption on an AMX membrane.²⁵ The results herein suggest that the reduced apparent OLC threshold voltage with reduced DNA concentration is due principally to variations in selectivity at lower voltages and that the decreased OLC conductivity (from the current-voltage slope in this region) is related to the reduced density of catalytic sites which can contribute to the second Wien effect. If so, the slope of the overlimiting region may be quantitatively correlated with the adsorbed surface DNA concentration, and an extension of the present study could help establish this. The dependence of transient response of the current-density components for the water ions on the density of ionogenic sites could also yield information regarding adsorbed surface DNA. It is critical to emphasize that these results are only qualitatively suggestive of the situation occurring at high DNA surface coverage. The low-coverage regime is inherently a three-dimensional problem with nanoscale features that can be expected to reveal a scale-dependent enhancement of the effect. The present results assume a 1D system with a typical size of about ~ 0.1 mm, whereas nanoscale features could be anticipated to have $\beta \sim 10$ and significantly lower onset of second Wien amplification. Such an effect might occur where sparse surface coverage of adsorbed DNA could result in highly localized field amplification, but may also involve strong electrohydrodynamic effects similar to those near charged polymer brushes.⁴⁷ Furthermore, nanoscale amplification of catalytic field-assisted dissociation may find use in other applications, for instance, involving molecular functionalization of nanopores.

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