

Polarization Effects at the Cation-Exchange Membrane – Solution Interface

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An experimental study of the concentration polarization effects at the cation-exchange membrane – solution interface has been carried out by means of a rotating diffusion cell. The set-up makes possible well-defined fluid mechanics. The effects are discussed mainly in terms of the current–voltage curves obtained. Possible transport mechanisms for over-limiting currents are also reviewed. The study of concentration polarization involves many basic concepts of transport theory, and has a number of technological implications.

The study of concentration polarization (CP) effects at the cation-exchange membrane – solution interface poses an interesting problem owing to both its academic background and its importance in the technology of ion exchange and desalination. CP develops in all membrane separation processes, as well as in electrode surfaces. This phenomenon has been extensively studied during recent decades in order to establish the factors which determine it and to solve the problems that polarization implies in particular technical applications. For example, one of the shortcomings preventing the widespread commercial use of electro-dialysis has been membrane polarization.¹ Thus an understanding of the early stages of polarization is necessary in order to develop methods by which it may be reduced.

The problem that arises when studying polarization in electrodialysis stacks is the complex hydrodynamics involved. Theoretical studies are commonly based on the so-called Nernst layer or modifications of this model.² The relevant parameter in this approach is the thickness of the unstirred layer, which can be determined from the hydrodynamics in the cell. However, since this parameter is usually unknown, it is not possible to compare theoretical and observed values of the limiting current density.

In this work, a rotating diffusion cell has been used to overcome this problem, since it involves well-defined[†] hydrodynamic conditions. Moreover, these conditions are appropriate for our study because the fluid velocity normal to the membrane is uniform in all planes parallel to the membrane surface. In this case, the problem of considering the thickness of the unstirred layer as a free parameter is eliminated, and the observed limiting values for the current

density can be compared with those predicted from the Nernst model. The cost we pay for using a rotating membrane cell is that some of the conclusions obtained may not be relevant to large-scale membrane processing.

In order to study CP processes in cation-exchange membranes we have registered the current–voltage (i – V) characteristics of these membranes, because their measurement is relatively easy and they contain much valuable information.

According to the classical CP theory,^{2,3} the i – V curve should be linear for low applied voltages, then increase slowly and finally reach a limiting value. In practice no such limiting value is observed, and the current density, after passing through a region of slow variation with potential, or simply through a point of inflection, continues to grow for high applied voltages. This implies that the limiting current density is an ill-defined parameter and must be obtained from indirect methods such as Cowan plots.⁴ The Cowan plot method will be used here to define the limiting current. Currents above the limiting one will be referred to as “over-limiting”.

In the first studies of this problem it was considered that the observed behaviour was only due to the contribution of ions coming from water dissociation. However, some more recent work has shown that these ions could contribute to this transport but never so as to explain the high current densities observed in cation-exchange membranes.⁵

This marked the beginning of a period in which researchers have been looking for a transport mechanism able to explain the i – V characteristics. Nowadays some of the proposed mechanisms have been ruled out, but there is no complete quantitative explanation for the problem. This fact is not surprising if we take into account that at high electric currents many of the hypotheses firmly rooted in

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[†]This fluid-mechanics problem has been solved by Levich.²

the classical theory of transport in ion-exchange membranes become doubtful. We will return to this question in the Discussion section.

Fundamentals

The theoretical basis of the rotating diffusion cell is the same as that for a rotating disc electrode.² The normal component of the fluid velocity (in cm s^{-1}) is given by eqn. (1), where ω is the rotation speed (in rad s^{-1}), v is the

$$v_z = 0.51 \omega^{3/2} \nu^{-1/2} z^2 \quad (1)$$

kinematic viscosity (in $\text{cm}^2 \text{s}^{-1}$) and z is the distance from the surface (in cm).

The thickness of the hydrodynamic boundary layer, δ_0 , is defined by considering that the tangential component of the fluid velocity, v_q , is reduced at $z = \delta_0$ to 5% of its value at the disc surface, $z = 0$. Then, eqn. (2) is obtained.

$$\delta_0 = 3.6 (v/\omega)^{1/2} \quad (2)$$

The concentration profile obtained from the solution of the convective diffusion equation leads to a diffusion layer thickness (in cm) given by eqn. (3),² where D is the salt

$$\delta_d = 1.612 D^{1/3} \nu^{1/6} \omega^{-1/2} \approx 0.05 \delta_0 \quad (3)$$

diffusion coefficient (in $\text{cm}^2 \text{s}^{-1}$). The theoretical limiting current density, i_l (A cm^{-2}), is given by eqn. (4), where

$$i_l = 2FD_c c_0 / \delta_d \quad (4)$$

D_c is the counterion diffusion coefficient in the solution phase, c_0 is the bulk solution concentration and a uni-univalent electrolyte has been considered.

There is one important point that has not been considered. The mathematical solution to the convective diffusion equation has been obtained with the boundary condition of zero solvent flow through the disc surface, as occurs in the case of a disc electrode; however, in the present situation we have a solvent flow through the membrane, i.e. electro-osmotic flow. This should lead to a modification of the profiles of the velocity components; however, preliminary calculations showed that such a modification is only minor, since the flux through the membrane is not high enough to produce a significant effect.

Experimental

Cell design. An Oxford Electrodes rotating diffusion cell was used, with small improvements made to allow for the exchange of the ion-exchange membranes and to the study different electrolyte solutions. The rotating cell was not employed as a diffusion cell, but as an electrolytic cell.

Usually, the membrane is glued to the rotating cylinder and then part of the membrane surface is collapsed to

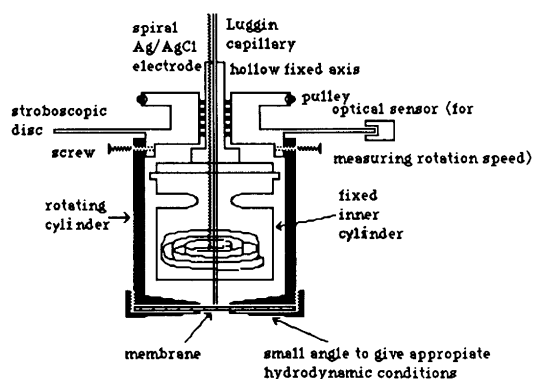


Fig. 1. Sketch of the rotating cell.

produce a well-defined active area. However, this is not possible with ion-exchange membranes (Ionics). Instead the membrane was directly mounted onto a bevelled annulus that was screwed to the rotating cylinder (Fig. 1).

Another problem with the previous design was the location of the electrodes (two silver strips of some 20 cm^2 surface area coated with silver chloride as current feed electrodes and two silver/silver chloride wires as reference electrodes). In the original diffusion cell there was insufficient room for these electrodes, so the reference electrodes were connected to the solutions near the membrane surface via Luggin capillaries. The conducting wires of the current feed electrodes were coated with PTFE. Details are shown in Fig. 2.

Finally, there were some problems with electrical noise owing to the small distance between the rotating cell and its driving motor. This noise was not easily avoidable, and we were only able to reduce the external noise by inserting the cell into a Faraday cage.

Materials and equipment. Solutions were prepared from Merck pro analysis grade chemicals (without further purification) and Milli-Q water. Ionics AZL cation-exchange membranes were used.

A PPR1 HI-TEK Instruments waveform generator and a PAR 173 potentiostat/galvanostat were used to pass current through the current electrodes. This current was measured through a resistance with a differential amplifier and recorded on a YEW X-Y recorder. A Haake D8-L thermostat

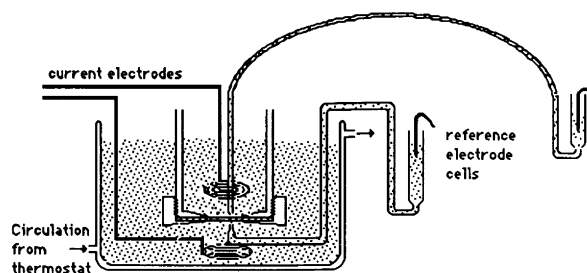


Fig. 2. Sketch of the electrode system.

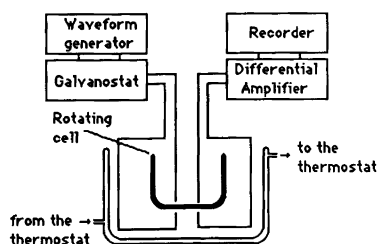


Fig. 3. Schematic diagram of the system used to obtain the i - V curves.

with a circulating pump and an Oxford Electrodes rotating diffusion cell were also employed.

Measurement of i - V curves. These curves are obtained either by applying a potential difference to the system and waiting for the current to reach a steady value or by imposing a current through the system and measuring the potential difference between the reference electrodes in the steady state. However, since the steady state is established in a few seconds, a slow continuous current sweep can be applied to the system by using a ramp generator and the time variation of the potential difference between the reference electrodes recorded. It is obvious that the last method is considerably faster and more practical; however, the sweep rate must be experimentally chosen so as to give virtually steady-state behaviour.

The membranes were soaked in concentrated solutions of the corresponding alkali chloride for several days before each experiment. Preceding each run, the membrane used was equilibrated for several hours with the solution employed in the experiment. This treatment was essential in order to eliminate water-splitting.⁶

All the runs were made in a thermostatted cell at 25.0°C. Fig. 3 shows a schematic diagram of the whole experimental set-up.

Results

Aqueous solutions of the sodium, lithium and potassium chlorides at three different concentrations, 30, 3 and 0.3 mM, were studied. i - V curves for these nine solutions were recorded in the stable (for which the upper working electrode is the negative electrode and the cation moves upwards through the horizontal membrane) and unstable (for which the cation moves downwards and instability may result) configurations.⁷ For each of these systems, the rotation frequency, $\bar{\nu}$, of the membrane was varied in the range 1–10 Hz.

A typical i - V curve is presented in Fig. 4. This curve was obtained for a 3 mM potassium chloride solution with 1 Hz rotation frequency and the current going upwards (stable configuration). The higher the rotation speed, the smaller the diffusion boundary layer (DBL) thickness and the higher the limiting current.² The i - V curve showed small changes when varying the bulk concentration, the current

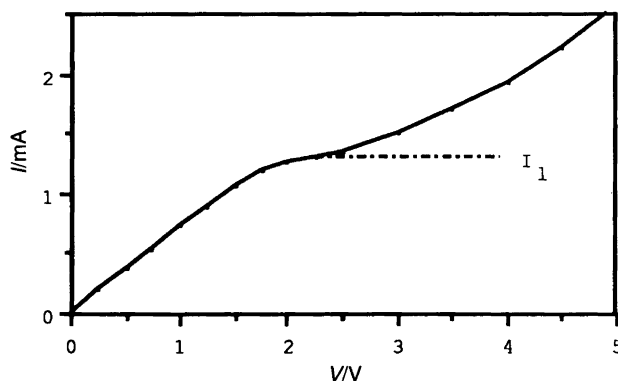


Fig. 4. Current vs. voltage curve obtained for 3 mM KCl, $\bar{\nu} = 1$ Hz and current going upwards. The discontinuous line indicates the limiting current according to the Cowan plot.

plateau being more pronounced for higher concentrations. Experimental evidence shows that the limiting current is proportional to the bulk solution concentration, as expected from theory. No distinctive features were observed when using other electrolyte solutions.

The limiting currents² have been determined by transforming the i - V curves into Cowan plots.⁴ This procedure consists of drawing tangents to the Cowan plot at the low current limit and in the first region of increasing resistance (development of a depleted layer near the membrane surface) and taking the limiting current as the current corresponding to the point of intersection of these two lines. A Cowan plot corresponding to the curve in Fig. 4 is presented in Fig. 5.

A comparison with Levich's results for the limiting current density at the electrode surface has been made by plotting the limiting current against the square root of the rotation speed.² The curves obtained in these plots (a typical one is shown in Fig. 6) were to a good approximation straight lines, although account should be taken of the relatively large errors involved in determining the limiting current. However, the slopes of the lines were different from those predicted by Levich's calculations. We always

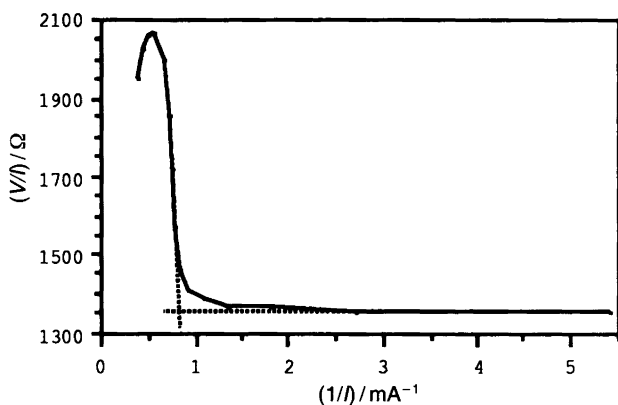


Fig. 5. Cowan plot corresponding to Fig. 4.

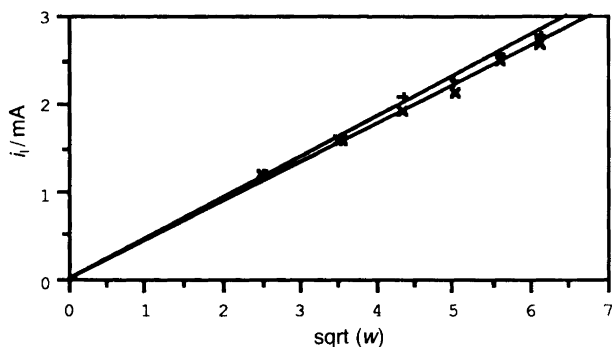


Fig. 6. Limiting current vs. square root of rotation speed [\sqrt{w}] for 3 mM KCl; +, $i_{l-d} = 0.459 \sqrt{w}$; X, $i_{l-u} = 0.442 \sqrt{w}$. d denotes current going downwards and u, current going upwards.

obtained diffusion-layer thicknesses larger than those given by eqn. (3). Very good agreement would have been obtained between the theoretical and observed limiting currents if the constant appearing in this equation were about 2 instead of 1.612.

This discrepancy between the observed value for the constant in eqn. (3) and the theoretical one has also been noted by Makai and Turner,⁸ although not so markedly. They refer to a paper by Gregory and Riddiford⁹ in which the latter showed that the constant depends upon the Schmidt number, being 1.612 for an infinitely large Schmidt number and slightly higher for realistic values of the Schmidt number. Nevertheless, it also seems possible to attribute this difference to an effective membrane surface effect. Note that we are evaluating the current density by dividing the current by the geometrical membrane area (1 cm^2).

The differences between the slopes of the lines in Fig. 6 when the current is passing upwards or downwards do not seem to be relevant, which is a surprising (see Discussion). The discrepancies observed in these values are much smaller than the experimental errors. In any case, it seems evident that diffusion control is always present, at least up to the limiting current density, otherwise the plots in Fig. 6 would not be linear.²

The i - V curves showed noise having the same frequency as the disc rotation frequency. This noise was quite uniform in the stable configuration but much more variable in amplitude in the unstable case. The relative amplitude of the noise was approximately 5%.

Finally, it is interesting to note that we did not observe pH changes during the runs. In fact, we chose the cation-exchange membranes and performed the soaking treatment so as to eliminate water-splitting.⁶ On the other hand, one can see that ca. 10^{-4} M of the ions arising from dissociation of water (H^+ , OH^-) would be necessary if over-limiting currents were to be transported by these ions.

Discussion: transport mechanisms for over-limiting currents

So far special attention has been paid to the so-called "limiting current". Many concepts from transport theory in charged membranes have been directly borrowed from the theory of electrolytic cells,² and this is the case for the limiting current. Strictly speaking, limiting currents do not exist in ion-exchange membranes (Fig. 4).

Despite the fact that many mechanisms have been proposed to explain the origin of the over-limiting currents during the last forty years, it is clear that a complete quantitative theory accounting for the whole i - V curve is still lacking. This situation is not surprising, since for currents beyond the limiting one a set of well-known hypotheses firmly established in the classical theory of membrane transport may become questionable (local electroneutrality, local equilibrium, negligible water-splitting, hydrodynamic stability etc.). We aim here to review briefly some of these hypotheses.

Co-ion leakage has sometimes been invoked as the origin of over-limiting currents. Although some earlier studies reported non-zero co-ion transport, the permselectivity of most commercial ion-exchange membranes in dilute salt solutions is around 90–100%, so that most measurements of co-ion transport numbers¹⁰ have shown the co-ion current to be a negligible contribution to the over-limiting current (at least as far as the stability of the fixed charge density on the membrane may be assured).

Since most studies on polarization are based on the Nernst model for the boundary layers, little attention has been paid to the role of *electro-osmotic convection* in the i - V curves. In practice, the flux equations considered do not normally contain a convective term. Although experimental³ and numerical simulation¹¹ studies have shown the electro-osmotic water transport to be negligible, it should be noted that some mechanisms of convection other than that of electro-osmotic origin can appear at high current densities. We will discuss this question later.

Another mechanism for over-limiting currents is that of *water-splitting*. It has been observed that when in the depleted layer the electrolyte concentration falls to extremely low values under the passage of high currents, H^+ and OH^- ions take part in the charge transport across the membrane¹² and pH changes appear in the layers adjacent to it. In practice, because of the high mobilities of these ions, their contribution to the total current becomes noticeable much earlier than the point at which their concentration in the boundary layer becomes locally comparable with that of the salt.¹³ Two conclusions can be drawn from water-splitting studies in ion-exchange membranes: first, the experimental evidence that this effect is much more common in anion-exchange membranes than in cation-exchange membranes;^{6,10} secondly, the well-known result that ordinary, equilibrium water dissociation taking place in the membrane-solution boundary layer cannot be responsible for the high over-limiting currents observed in anion-ex-

change membranes.^{14,15} The strong electric fields generated at the membrane–solution interface can give rise to water-splitting through the second Wien effect or, more probably, through specific chemical reactions related to the fixed charge groups in the membrane.^{15,16}

Theoretical models predict that the introduction of the *local equilibrium* assumption for the membrane–solution interface would be justified only in the limit of small fluxes.¹⁷ The state of this interface during ion transport is not known with certainty, although some theoretical^{17–19} and experimental^{20,21} studies have analyzed the question. Departures from local equilibrium seem to be small in the case of film control,¹⁸ being larger for co-ion than for counterion transport, and showing a decrease as the selectivity of the membrane increases.¹⁹ Although the above conditions seem to support the local equilibrium assumption in ion-exchange membranes, it is clear that this question deserves more attention. Indeed, according to the classical theory of membrane electrochemistry,³ we have a region (the interface), that is very small in size when compared to the membrane, and this in itself invites us to neglect it. This intuitive reasoning, together with more rigorous studies,²² has originated the frequent omission of a detailed study of the membrane–solution interface in the ion-exchange literature. This situation seems to be changing now,^{7,14,15,17–20} although the fundamental interfacial electrochemistry of the electric double layer at the polymer–water interface²³ is not so well understood as the double layers at the metal–aqueous electrolyte and liquid–liquid interfaces.

The classical theory of CP² assumed *local electroneutrality* in the diffusion boundary layers and was self-consistent at currents lower than the limiting one, i.e. the charge density evaluated via the Poisson equation was negligible for small currents. However, a considerable amount of space charge would appear at the electrode–solution interface if the limiting current were reached. Levich² used this argument to establish that over-limiting currents could not be observed through a metal–solution interface.

This question is not so clear when dealing with membrane–solution interfaces. Thus, Rubinstein *et al.*^{24–27} have considered the formation of a region of space charge near the membrane as a conduction mechanism which would account for over-limiting currents. Although this formulation of the problem is interesting, the theoretical treatment leads to extremely high charge densities over large, *macroscopic* regions.^{24–26} This result arises from the boundary condition $c_+(\delta+) = \bar{X}$, where $c_+(\delta+)$ is the local counterion concentration just within the membrane and \bar{X} is the fixed-charge concentration in the membrane. (Here $x = \delta$ denotes the point at which the membrane–solution interface is located, so that $\delta+$ stands for the membrane (inner) part of the interface and $\delta-$ for the solution (outer) part of this interface). Note that this boundary condition, corresponding to the *inner* part of the membrane–solution interface, is being imposed on the solution of a set of equations written down to describe the transport *within* the DBL far away from the interface.²⁴ It is just this boundary

condition which causes the space-charge density to reach extremely high values and spread out from the membrane–solution interface to the macroscopic DBL (e.g. Fig. 4, Ref. 24). Again, as in the case of the local equilibrium assumption, we are facing the problem of describing transport through a region (the interface) whose small size has “justified” the omission of a detailed study in many practical cases.

However, the study of deviations from local electroneutrality at high CP has a clear, intuitive motivation: different experimental analyses^{5,12,28,29} have shown that under a high electric current the local salt concentration in the zone of the DBL just outside the membrane ($x = \delta-$) can drop to the order of 10^{-5} – 10^{-4} M. Taking this into account, it can be shown that the local electroneutrality condition breaks down for $i \approx i_l$. Indeed, a direct calculation based on the Nernst–Planck equation for the ion fluxes and the Poisson equation (replacing the local electroneutrality condition) for the space charge leads to eqn. (5) for the local concentration “just outside” the membrane interface,

$$c(\delta-) = \frac{c_+(\delta-) + c_-(\delta-)}{2} = c_0 \left(1 - \frac{i}{i_l} \right) + \frac{\epsilon}{RT} (E^2(\delta-) - E^2(0)) \quad (5)$$

where ϵ is the solution dielectric constant, c_0 the bulk solution concentration, i_l is the limiting current density and E is the local electric field at the points $x = 0$ and $x = \delta-$ delimiting the DBL. According to experiment,^{5,12,28,29} for $i \approx i_l$, $c(\delta-) \approx 10^{-4}$ M, and then $E(\delta-) \approx (10^5 - 10^6)$ V m⁻¹. Now, if we take the ratio between the local electrical U_E and thermal U_T volumetric energies at $x = \delta-$, we have

$$\left(\frac{U_E}{U_T} \right)_{x=\delta-} = \frac{\frac{1}{2} \epsilon E^2(\delta-)}{RTc(\delta-)} \approx 1. \quad (6)$$

eqn. (6). Then, a simple order-of-magnitude analysis shows that the local electroneutrality condition seems to break down just outside the membrane interface for $i \approx i_l$, as suggested by Levich and Rubinstein *et al.*

Although some results of Refs. 24–27 may be questionable, the implicit idea that a careful study of the *system stability* for high CP^{7,27} should be undertaken merits more attention. Indeed, it has been mentioned that the rapid current rise beyond the plateau in the high polarization regime of the i – V curve cannot be ascribed to any *defect of permselectivity*,²⁸ but to a violent convection being set up near the membrane surface for $i \approx i_l$. Convection at the membrane surface might occur as a consequence of an unknown *hydrodynamic instability*, and this effect has been reported in many experimental studies^{7,10,30,31} and has sometimes been ascribed either to a superposition of concentration and temperature gradients or to local mixing of the DBL by electroconvection.⁷ The noise spectra generated during ion transport across membranes have also been

measured in a series of papers by Lifson *et al.*³¹ and by Green and co-workers,³²⁻³⁵ and contributions to the noise from high current instabilities causing hydrodynamic turbulence have been detected. However, a complete quantitative theory accounting for all the observed phenomena is still lacking. Note that convective motions produced in a fluid when only one property affects the density are very well understood, but the situation changes drastically when gradients of more than one diffusion property are relevant. In fact, a set of new phenomena can appear in this case,³⁶ and extensions of the classical Nernst model to describe the over-limiting current effects,³⁷ while of interest, may only be valid for qualitative purposes.³⁸

The basic idea seems to be that in the DBL the concentration and temperature gradients* create a density gradient which causes hydrodynamic convection currents. For high enough currents this convection becomes turbulent. In this regime, introduction of the simple Nernst-Planck equation, together with extension of the Nernst model, is an over-simplifying procedure.

It should be mentioned that a remarkable result for over-limiting current is a characteristic low-frequency noise of some 1–10 Hz.^{7,31} This noise is attributed to turbulent currents injecting salt into the depleted DBL. The turbulent currents cause fluctuations in the electrical resistance of this layer, and this leads to the observed noise in the i - V curve.^{7,31} Note also that injection of this salt causes the concentration term $c(\delta-)$ to depart from zero, corresponding to i_i ,^{2,3} thus allowing for the onset of over-limiting currents.

If the latter interpretation of the low-frequency noise is correct, it seems possible in principle to estimate the concentration $c(\delta-)$ at currents near the limiting value. Indeed, we can write eqn. (7), a simplified balance equation for the DBL, where A is the effective membrane area,

$$c(\delta-) \frac{A \delta}{\tau_{\text{noise}}} \approx Ai/F \quad (7)$$

δ the DBL thickness and τ_{noise} the characteristic time required for turbulent currents to renew the depleted salt concentration in the layer. According to experimental data, $\delta \approx 10^{-2}$ cm, $i \approx 1$ mA cm⁻² and $\tau_{\text{noise}} \approx 10^{-1}$ s, which leads to $c(\delta-) \approx 10^{-4}$ M. This value is in agreement with the experimental findings of Refs. 12, 28 and 29.

It is well known that far from equilibrium, bifurcations and multiple steady states can appear, especially in biophysical systems.³⁹ Negative fluctuations can destroy a given steady state and lead to a new one. Rubinstein⁴⁰ has recently initiated the study of i - V curves for the case of multiple steady states in one-dimensional electrodiffusion

* A concentration gradient within the diffusion boundary layer establishes a gradient in the electrical resistance through this layer. Thus, non-uniform heating effects may appear under passage of an electric current.

with local electroneutrality. This may provide a new procedure for examining the problem of over-limiting currents.

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