MASS TRANSPORT THROUGH CHARGED MEMBRANES

Dieter Bothe and Jan Prüss

Fachbereich Mathematik und Informatik, Universität-GH Paderborn Warburger Str. 100, D-33098 Paderborn, Germany, Email: dieterb@uni-paderborn.de

Fachbereich Mathematik und Informatik, Martin-Luther-Universität Halle-Wittenberg Theodor-Lieser Str. 5, D-60120 Halle, Germany, anokd@volterra.mathematik.uni-halle.de

Abstract

A modern technique for desalination or softening of water is the so-called *nanofiltration* by means of membranes which carry a fixed electric charge. For the mathematical modeling of such processes, two features are particularly important. Firstly, the distribution of ionic species generates an electric field which in turn affects the fluxes of these ions. Therefore, besides diffusion and convection, *electromigration* has to be taken into account. This also leads to a strong coupling of the concentrations of all charged species, which can often be adequately incorporated into the model via the assumption of *electroneutrality*. Secondly, electrical double-layers (*Donnan potential*) build up at the surface of the membrane, which cause discontinuities in the ionic concentration profiles.

We deduce a mathematical model for such a nanofiltration process. This leads to a strongly coupled quasilinear parabolic system with nonlinear transmission and dynamical boundary conditions. By means of degree theory we obtain existence of stationary solutions, while L^p-maximal regularity is employed to get local strong wellposedness of this model.

AMS Classifications

Primary: 34B60, 35K50, 92E20
Secondary: 35K60, 35Q80, 47H11, 78A35

Key Words and Phrases

diffusion-migration system, electroneutrality, quasilinear parabolic system, dynamical boundary condition, degree theory, maximal regularity, nanofiltration

Running Head: Mass Transport Through Charged Membranes

1. Introduction.

Nanofiltration is a pressure driven separation process that employs specific membranes consisting of a polymeric matrix which carries fixed ionic groups. If the void space of such a membrane is filled with an aqueous solution these groups dissociate by separation of mobile ions like protons or hydroxide ions. Since the latter enter the aqueous phase, a fixed electric charge inside the polymeric matrix remains. Due to the fact that ionic solutions are electrically neutral on the macroscopic scale, this leads to a considerable change of the composition inside the membrane, compared to the adjacent bulk phases. This effect forms the heart of nanofiltration processes and allows for the selective removal of ionic species with multiple charges like calcium, magnesium, sulfate, phosphate etc.

For technically relevant filtration processes sufficiently high flow rates across the membrane are necessary which require a large surface of the membrane. A common way to achieve this within a reasonable volume is to pile up several membranes in so-called disc-tube modules. Such modules are constructed in such a way that the feed solution flows tangentially along one membrane after the other. A certain amount of the solution is pressed through the membrane to yield the desired *permeate*, while the remaining fluid collects the rejected ions and leaves the system as so-called *retentate* with higher concentrations. By means of this cross-flow operation, blockage of the membrane due to precipitation is avoided. Still, a thin film of microorganism will settle down on the surface of the membrane, a problem present in any aqueous system. This fouling slows down mass transport and leads to increased concentrations of ions inside the permeate phase. In fact, the rejection rate then decreases for large pressure differences.

Concerning the intensification of such nanofiltration processes, a fundamental understanding based on mathematical models is essential. For more detailed information concerning the technical background see [6] and in particular [5].

2. Mathematical Modeling.

We develop a mathematical model that incorporates the relevant mass transport phenomena mentioned above, while appropriate simplifications concerning the hydrodynamics are introduced. To be specific, we suppose the bulk phases containing retentate or permeate to be ideally mixed and assume stationary hydrodynamics. The latter implies

$$\dot{V}^f = \dot{V}^R + \dot{V}^P,$$

where $\dot{V}^j$ denotes the volumetric flow rate for $j = f$ (*feed*), R (*retentate*) or P (*permeate*), respectively.

We consider a single planar membrane carrying a feed-sided film inside of which the species have reduced mobility. The latter represents a combination of the biofilm mentioned above and a hydrodynamic boundary layer (the so-called Nernst boundary layer). Since the concentrations inside ideally mixed bulk phases are homogeneous, mass transport across the membrane is solely oriented in the normal direction as illustrated by Figure 1.

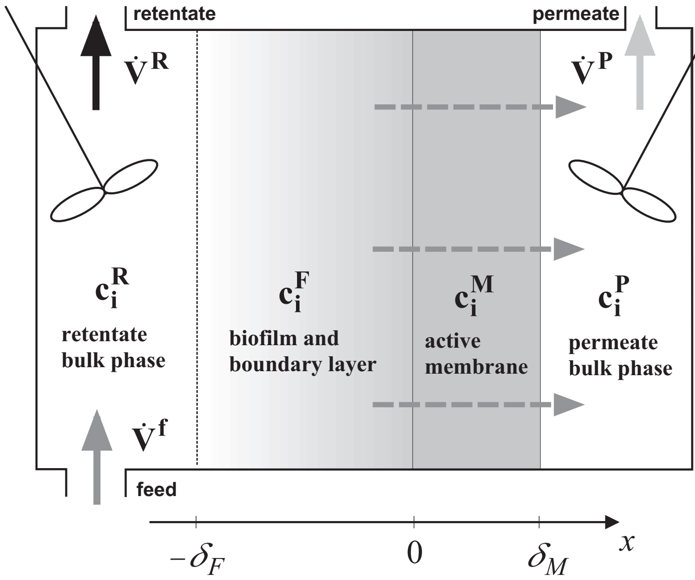

Figure 1

Consequently, the mathematical model involves only one spatial dimension. Mass balances for all species implies

$$
\begin{array}{lll}
\text{retentate :} & \dfrac{d}{dt}(V^R c_i^R) = \dot{V}^f c_i^f - \dot{V}^R c_i^R - A^F J^F_{i|x=-\delta_F} & t > 0 \\
\text{biofilm :} & \dfrac{\partial}{\partial t} c_i^F + \operatorname{div} J_i^F = 0 & t > 0, \quad -\delta_F < x < 0 \\
\text{membrane :} & \dfrac{\partial}{\partial t} c_i^M + \operatorname{div} J_i^M = 0 & t > 0, \quad 0 < x < \delta_M \\
\text{permeate :} & \dfrac{d}{dt}(V^P c_i^P) = -\dot{V}^P c_i^P + A^M J^M_{i|x=\delta_M} & t > 0
\end{array}
\tag{1}
$$

Here we use the following notation: subscripts denote the species number, while superscripts indicate the corresponding phase. Hence c_i^j means concentration of species i inside phase j, V^j are the bulk volumes and A^j is the interfacial area between phase j and the adjacent bulk phase. So, in the sequel all the hydrodynamic quantities like the volume fluxes $\dot{V}^j$, the bulk volumes V^j, the interfacial areas A^j as well as the film and membrane diameters δ_j are positive constants.

In electrochemical systems, mass fluxes of charges species are not only due to convection and diffusion. The distribution of charges creates an electrical field which causes additional electromigration of ions. A commonly accepted constitutive equation for the fluxes (see [7]) is given by

$$J_i^j = -D_i^j \frac{\partial}{\partial x} c_i^j + v^j c_i^j - \frac{F}{RT} D_i^j z_i c_i^j \frac{\partial}{\partial x} \phi^j \quad (j = F, M), \tag{2}$$

where $D_i^j > 0$ denote the diffusivities, v^j the convective speed of the solvent, z_i the charge numbers and ϕ^j the electric potential. Furthermore F is the Faraday constant, R the universal gas constant and T the absolute temperature. Let us note in passing that the Nernst-Einstein equation, relating the mobility of ions to their diffusivity, has already been incorporated into (2) for technical simplicity.

To obtain a closed model, an equation for the electric potential has to be added. If electrodynamical effects are neglected, a reasonable choice would be the Poisson equation

$$\Delta \phi^j = -\frac{F}{\epsilon} \sum_{i=1}^{n} z_i c_i^j,$$

where ϵ is the permittivity of the electrolyte solution. Unfortunately, accurate boundary conditions for ϕ^j are hard to get and ϵ depends on the composition of the electrolyte in a complicated, often unknown way. On the other hand, on the macroscopic scale the solution is electrically neutral to a high degree of accuracy inside bulk phases. Mathematically this corresponds to the fact that F/ϵ has a very large value. Therefore we add the condition of electroneutrality, i.e. the algebraic constraint

$$\sum_{i=1}^{n} z_i c_i^j = \begin{cases} 0 & \text{if } j = R, F, P \\ c_0^M & \text{if } j = M. \end{cases} \tag{3}$$

Equation (3) refers to membranes with fixed negative charges in which case c_0^M denotes an equivalent concentration of negative ions with charge number -1.

Finally, the model has to be complemented by boundary and transmission conditions. These are continuity of the fluxes and continuity of the electrochemical potentials. While the former directly translates into

$$J_i^F(0) = J_i^M(0) \qquad \text{for } i = 1, \ldots, n, \tag{4}$$

the latter needs some more explanation. The electrochemical potential $\bar{\mu}_i$ of a species i is given by

$$\bar{\mu}_i = \mu_i^0 + RT \ln a_i + z_i F \phi,$$

where μ_i^0 is the chemical standard potential and a_i is the activity. For dilute solutions a_i can be replaced by the concentration c_i which will be done in the sequel. At interfaces where ϕ is continuous this implies continuity of the concentrations, i.e.

$$c_i^R = c_i^F(-\delta_F) \qquad \text{for } i = 1, \ldots, n. \tag{5}$$

The same can not be true at the surfaces of the membrane, since this would not be consistent with electroneutrality. At the film-sided interface, continuity of the electrochemical potential yields

$$\ln c_i^F(0) + \frac{F}{RT} z_i \phi^F(0) = \ln c_i^M(0) + \frac{F}{RT} z_i \phi^M(0),$$

hence

$$c_i^M(0) = c_i^F(0) e^{\alpha z_i} \qquad \text{with } \alpha = \frac{F}{RT}(\phi^F(0) - \phi^M(0)).$$

Electroneutrality inside the membrane yields

$$\sum_{i=1}^n z_i c_i^F(0) e^{\alpha z_i} = c_0^M,$$

which uniquely defines α for all compositions such that $c_i^F(0) > 0$ for some i with $z_i \neq 0$; notice that $\psi(\alpha) = \sum_{i=1}^n z_i c_i e^{\alpha z_i}$ is strictly increasing such that $\lim_{\alpha \to \pm\infty} \psi(\alpha) = \pm\infty$, then. Observe also that $\alpha \neq 0$ in case $c_0^M \neq 0$ which is physically comprehensible: due to the fixed negative charge density inside the membrane, an electrical double layer builds up at the surface. On the macroscopic scale this leads to a discontinuity of the electric potential which causes a jump in the concentration profiles of charged species. The difference $\phi^F(0) - \phi^M(0)$ is the so-called *Donnan potential.* Since the same arguments apply at the interface between membrane and permeate, we obtain the conditions

$$c_i^M(0) = c_i^F(0)\, g_i^F(c^F(0)), \quad c_i^M(\delta_M) = c_i^P\, g_i^P(c^P) \tag{6}$$

with function g_i^F, g_i^P implicitly given by

$$g_i^F(c) = e^{\alpha z_i} \;\text{ iff }\; \sum_{i=1}^n z_i c_i e^{\alpha z_i} = c_0^M, \qquad g_i^P(c) = e^{\beta z_i} \;\text{ iff }\; \sum_{i=1}^n z_i c_i e^{\beta z_i} = c_0^M. \tag{7}$$

In summary, the complete model has the form of a partial differential-algebraic system consisting of the balance equations (1) with fluxes given by (2), the transmission and boundary condition (4), (5), (6) and the algebraic condition (3) of electroneutrality.

There are only few papers about electrochemical systems in the mathematical literature. While results for related problems from electrolysis can be found in [1], [2], [8] and [9], rigorous investigations of membrane processes including the appearance of Donnan potentials are apparently missing.

3. The Stationary Problem.

In the stationary case the transport equations in (1) reduce to div $J_i^j = 0$, hence by continuity of the mass fluxes and (1), they satisfy

$$J_i^F(x) \equiv v^P c_i^P \quad (-\delta_F < x < 0), \qquad J_i^M(x) \equiv v^P c_i^P \quad (0 < x < \delta_M)$$

with $v^P := \dot{V}^P/A^M$. Then (2) yields

$$-\frac{\partial}{\partial x}c_i^j + \frac{v^j c_i^j}{D_i^j} - z_i c_i^j \frac{F}{RT}\frac{\partial}{\partial x}\phi^j = \frac{v^P c_i^P}{D_i^j} \quad (j = F, M).$$

Multiplication with z_i and summation over all species, accounting for electroneutrality, gives

$$\frac{F}{RT}\left(\frac{\partial}{\partial x}\phi^j\right)\sum_{i=1}^n z_i^2 c_i^j = \sum_{i=1}^n z_i \frac{v^j c_i^j - v^P c_i^P}{D_i^j} \quad (j = F, M).$$

This allows for elimination of the electrical field from the mass fluxes. Together with the remaining retentate balance as well as (5) and (6), we obtain the following boundary value problem. For clarity, we use the abbreviations

$$\mathbf{c}^j = (c_1^j, \ldots, c_n^j), \quad \mathbf{D}^{-j} = \operatorname{diag}(1/d_1^j, \ldots, 1/d_n^j), \quad \mathbf{z} = (z_1, \ldots, z_n) \quad \mathbf{Z} = \operatorname{diag}(z_1, \ldots, z_n).$$

With this condensed notation, the stationary problem reads as

$$\begin{aligned} \frac{\partial}{\partial x}\mathbf{c}^F &= \mathbf{D}^{-F}(v^F\mathbf{c}^F - v^P\mathbf{c}^P) - \frac{\langle \mathbf{z}, \mathbf{D}^{-F}(v^F\mathbf{c}^F - v^P\mathbf{c}^P)\rangle}{\langle \mathbf{z}, \mathbf{Z}\,\mathbf{c}^F\rangle}\mathbf{Z}\mathbf{c}^F \qquad & -\delta_F < x < 0 \\ \frac{\partial}{\partial x}\mathbf{c}^M &= \mathbf{D}^{-M}(v^M\mathbf{c}^M - v^P\mathbf{c}^P) - \frac{\langle \mathbf{z}, \mathbf{D}^{-M}(v^M\mathbf{c}^M - v^P\mathbf{c}^P)\rangle}{\langle \mathbf{z}, \mathbf{Z}\,\mathbf{c}^M\rangle}\mathbf{Z}\mathbf{c}^M \qquad & 0 < x < \delta_M \end{aligned} \tag{8}$$

with boundary and transmission conditions

$$\begin{aligned} \mathbf{c}^F(-\delta_F) &= \mathbf{c}^R \\ \mathbf{c}^M(0) &= \mathbf{c}^F(0)\cdot\mathbf{g}^F(\mathbf{c}^F(0)) \\ \mathbf{c}^M(\delta_M) &= \mathbf{c}^P\cdot\mathbf{g}^P(\mathbf{c}^P) \\ \dot{V}^f\mathbf{c}^f &= \dot{V}^R\mathbf{c}^R + \frac{A^F}{A^M}\dot{V}^P\mathbf{c}^P, \end{aligned} \tag{9}$$

where a dot stands for componentwise multiplication.

Theorem 1. *For a given nonnegative and electroneutral feed composition $\mathbf{c}^f$ the stationary problem (8), (9) has a nonnegative classical solution.*

Proof. If the feed contains no charged species, then the problem is a purely diffusional one. This case is much simpler and will not be discussed here. Hence we assume that $c_i^f > 0$ for some index i with $z_i \neq 0$.

We reduce to a fixed-point problem, where it is favorable to solve the differential equations backwards, since $\mathbf{c}^P$ is involved in the boundary condition and appears on the right-hand sides in (8).

Given any permeate composition $\mathbf{c}^P \geq 0$ such that $\langle \mathbf{z}, \mathbf{c}^P\rangle = 0$ and $c_i^P > 0$ for some i with $z_i \neq 0$, the permeate-sided membrane concentration $\mathbf{c}^M(\delta_M)$ is uniquely determined by (9). Notice that $\mathbf{c}^M(\delta_M) \geq 0$ depends continuously on $\mathbf{c}^P$ with $c_i^M(\delta_M) > 0$ iff $c_i^P > 0$. For this initial value, the second ODE-system in (8) has a unique backward solution up to $x = 0$. Indeed, the right-hand side is locally Lipschitz continuous with at most linear growth in $\mathbf{c}^M$. Hence a unique local solution exists as long as $\langle \mathbf{z}, \mathbf{Z}\,\mathbf{c}^M \rangle > 0$. The latter holds on all of $[0, \delta_M]$ if the solution stays nonnegative, since $\langle \mathbf{z}, \mathbf{c}^M(\delta_M) \rangle = c_0^M$ together with $\frac{\partial}{\partial x} \langle \mathbf{z}, \mathbf{c}^M \rangle = 0$ implies

$$c_0^M = \sum_{i=1}^n z_i c_i^M \leq \sum_{i=1}^n |z_i| c_i^M \leq \sum_{i=1}^n z_i^2 c_i^M.$$

The solution stays in fact nonnegative, since $\mathbf{c}^M(x_0) \geq 0$ and $c_i^M(x_0) = 0$ imply

$$\frac{\partial}{\partial x} c_i^M(x_0) = -\frac{v^P c_i^P}{D_i^M} \leq 0.$$

The same argument yields $c_i^M(0) > 0$ iff $c_i^P > 0$.

To pass to the film, we rewrite the transmission condition at $x = 0$ as

$$c_i^F(0) = c_i^M(0) e^{-\alpha z_i} \quad \text{with } \alpha \text{ such that } \sum_{i=1}^n z_i c_i^M(0) e^{-\alpha z_i} = 0.$$

Therefore $\mathbf{c}^P \geq 0$ continuously determines a unique $\mathbf{c}^F(0) \geq 0$ such that $\langle \mathbf{z}, \mathbf{c}^F(0) \rangle = 0$ and $c_i^F(0) > 0$ iff $c_i^P > 0$. As similar reasoning as given above shows that the first ODE-system in (8) with this initial value has a unique backward solution up to $x = -\delta_F$. Here $\gamma(x) = \sum_{i=1}^n c_i^F(x)$ satisfies

$$\gamma'(x) \leq \frac{v^F}{\min_i D_i^F} \gamma(x) - \frac{v^P}{\max_i D_i^F} \sum_{i=1}^n c_i^P,$$

hence the solution exists up to $x = -\delta_F$ and $c_i^F(-\delta_F) > 0$ iff $c_i^P > 0$.

Let $F(\mathbf{c}^P)$ denote the vector $\mathbf{c}^R = \mathbf{c}^F(-\delta_F)$ determined by $\mathbf{c}^P$ this way. To sum up,

$$F : D(F) = E \cap \{\mathbf{c} \in \mathbb{R}_+^n : \langle \mathbf{z}, \mathbf{Z}\mathbf{c} \rangle > 0\} \to E \cap \mathbb{R}_+^n \quad \text{with } E = \{\mathbf{c} \in \mathbb{R}^n : \langle \mathbf{z}, \mathbf{c} \rangle = 0\} \tag{10}$$

is continuous with $F_i(c) > 0$ iff $c_i > 0$. Moreover, the above constructed solutions evidently solve the stationary problem (8), (9) iff $\mathbf{c}^P$ satisfies

$$\mathbf{c}^P = \frac{A^M}{A^F} \Big(\frac{\dot{V}^f}{\dot{V}^P} \mathbf{c}^f - \frac{\dot{V}^R}{\dot{V}^P} F(\mathbf{c}^P) \Big). \tag{11}$$

We shall apply degree theory to obtain a solution of this fixed-point problem, where we work in the Banach space E (with $\mathbb{R}^n$-norm). Let

$$\bar{\mathbf{c}} = \frac{A^M \dot{V}^f}{A^F \dot{V}^P} \mathbf{c}^f, \quad G(\mathbf{c}) = \bar{\mathbf{c}} - \frac{A^M \dot{V}^R}{A^F \dot{V}^P} F(\mathbf{c})$$

and

$$\Omega = \{\mathbf{c} \in E : 0 < c_i < \bar{c}_i, \sum_{z_k \neq 0} c_k > \eta\},$$

where $\eta > 0$ is to be chosen later. Evidently Ω is open bounded convex and G is continuous on $\bar{\Omega}$. To obtain existence of a fixed-point of G we shall use homotopy invariance of the degree (cf. [3]) to pass to a simpler problem. For this purpose we define a homotopy $H(\mathbf{c}^P, \lambda)$ as follows. Replace

$$\begin{gathered} D_i^j \text{ by } D_i^j(\lambda) = (1-\lambda) + \lambda D_i^j \quad (j = F, M), \\ v^j \text{ by } v^j(\lambda) = (1-\lambda)v^P + \lambda v^j \quad (j = F, M), \\ c_0^M \text{ by } c_0^M(\lambda) = \lambda c_0^M. \end{gathered}$$

Given $\lambda \in [0,1]$ and $\mathbf{c}^P \geq 0$, repetition of the above arguments yields a corresponding $\mathbf{c}^R$ which gives $F(\mathbf{c}^P, \lambda) := \mathbf{c}^R$. We then define the homotopy H by

$$H(\mathbf{c}^P, \lambda) = \bar{\mathbf{c}} - \frac{A^M \dot{V}^R}{A^F \dot{V}^P} F(\mathbf{c}^P, \lambda).$$

Obviously $H(\cdot, \cdot)$ is continuous due to the continuous dependence of the solutions of (8) on the parameters and initial values. We claim that $H(\cdot, \lambda)$ has no fixed-point on $\partial\Omega$ if $\eta > 0$ is sufficiently small. Assume that $H(\mathbf{c}^P, \lambda) = \mathbf{c}^P$ for some $\lambda \in [0,1]$ and $\mathbf{c}^P \in \bar{\Omega}$. If $\mathbf{c}^P \in \partial\Omega$ then there are three possible cases.

(i) There exists some i such that $c_i^P = 0$. Then $F_i(\mathbf{c}^P, \lambda) = 0$ yields the contradiction $H_i(\mathbf{c}^P, \lambda) = \bar{c}_i > c_i^P$.

(ii) There exists some i such that $c_i^P = \bar{c}_i$. Then $F_i(\mathbf{c}^P, \lambda) > 0$ yields the contradiction $H_i(\mathbf{c}^P, \lambda) = \bar{c}_i - F_i(\mathbf{c}^P, \lambda) < c_i^P$.

(iii) The remaining case $\sum_{z_k \neq 0} c_k^P = \eta$ needs some preparation. Below we use the abbreviations

$$z_k^+ = \max\{z_k, 0\}, \;\; z_k^- = \max\{-z_k, 0\}, \;\; z_{\max}^+ = \max_k z_k, \;\; z_{\max}^- = \max_k(-z_k),$$
$$v_{\max} = \max\{v^F, v^M, v^P\}, \;\; d^j = \min\{1, D_1^j, \ldots, D_n^j\};$$

observe that $D_i^j(\lambda) \geq d^j$ holds for any $\lambda \in [0,1]$. Let

$$\rho = \frac{\dot{V}^f}{\dot{V}^R} \sum_{z_k \neq 0} c_k^f > 0, \quad \sigma = \frac{A^F \dot{V}^P}{A^M \dot{V}^R} > 0,$$

notice that

$$\sum_{z_k \neq 0} c_k^R = \sum_{z_k \neq 0} F_k(\mathbf{c}^P, \lambda) = \rho - \sigma \sum_{z_k \neq 0} c_k^P = \rho - \sigma\eta$$

and recall $\langle \mathbf{z}, \mathbf{c}^R \rangle = 0$. Hence

$$\rho - \sigma\eta = \sum_{z_k \neq 0} c_k^R \leq \sum_{z_k > 0} z_k c_k^R + \sum_{z_k < 0} c_k^R \leq \sum_{z_k < 0} c_k^R (1 + z_{\max}^-)$$

shows that there exists some i such that

$$z_i < 0 \ \text{ and } \ c_i^R = c_i^F(-\delta_F) \geq \frac{\rho - \sigma\eta}{n(1+z_{\max}^-)}. \tag{12}$$

We fix this index i and use differential inequalities to get the contradiction $c_i^P > \eta$ for small $\eta > 0$. Due to $z_i < 0$, the ODEs (8) imply

$$\begin{aligned}
\frac{\partial}{\partial x}\, c_i^j &\geq \frac{v^j(\lambda)c_i^j - v^P c_i^P}{D_i^j(\lambda)} + \frac{-z_i c_i^j}{\sum_{k=1}^n z_k^2 c_k^j}\Big(v^j(\lambda)\sum_{z_k<0}\frac{z_k c_k^j}{D_k^j(\lambda)} - v^P \sum_{z_k>0}\frac{z_k c_k^P}{D_k^j(\lambda)}\Big)\\
&\geq \frac{v^j(\lambda)c_i^j - v^P c_i^P}{D_i^j(\lambda)} - z_i c_i^j v^j(\lambda)\frac{\sum_{z_k<0} z_k c_k^j/D_k^j(\lambda)}{\sum_{k=1}^n |z_k| c_k^j} - \frac{v^P z_{\max}^+}{d^j}\,\eta\\
&\geq \frac{v^j(\lambda)c_i^j}{D_i^j(\lambda)} + z_i c_i^j v^j(\lambda)\frac{\sum_{z_k<0} |z_k| c_k^j/D_k^j(\lambda)}{\sum_{z_k<0}^n |z_k| c_k^j} - \frac{v^P(1+z_{\max}^+)}{d^j}\,\eta\\
\geq \frac{v^j(\lambda)c_i^j}{D_i^j(\lambda)} &+ \frac{z_i c_i^j v^j(\lambda)}{d^j} - \frac{v^P(1+z_{\max}^+)}{d^j}\,\eta \geq -\frac{v_{\max} z_{\max}^-}{d^j}\,c_i^j - \frac{v^P(1+z_{\max}^+)}{d^j}\,\eta,
\end{aligned}$$

hence

$$\frac{\partial}{\partial x}\, c_i^j \geq -a^j c_i^j - b^j\eta \quad \text{ with } a^j = \frac{v_{\max} z_{\max}^-}{d^j},\ b^j = \frac{v^P(1+z_{\max}^+)}{d^j}.$$

Consequently,

$$\begin{aligned}
c_i^F(x) &\geq c_i^F(-\delta_F)e^{-a^F(x+\delta_F)} - \eta\, b^F/a^F \qquad && \text{on } [-\delta_F, 0]\\
c_i^M(x) &\geq c_i^M(0)e^{-a^M x} - \eta\, b^M/a^M && \text{on } [0, \delta_M].
\end{aligned}$$

By means of (12) we obtain

$$c_i^F(0) \geq e^{-a^F\delta_F}\frac{\rho - \sigma\eta}{n(1+z_{\max}^-)} - \eta\frac{b^F}{a^F},$$

hence there is $\eta_0 > 0$ such that

$$c_i^F(0) \geq \frac{\rho e^{-a^F\delta_F}}{2n(1+z_{\max}^-)} \tag{13}$$

whenever $0 < \eta < \eta_0$. To pass to the membrane, we need an estimate from above for α. Exploitation of (6), (3) and $c_0^M \geq c_0^M(\lambda)$ as well as $\alpha \geq 0$ yields

$$c_0^M \geq \sum_{k=1}^n z_k c_k^F(0)e^{\alpha z_k} = \sum_{k=1}^n c_k^F(0) z_k(e^{\alpha z_k} - 1) \geq c_l^F(0) z_l(e^{\alpha z_l} - 1) \ \text{ for any } l. \tag{14}$$

To obtain an appropriate index l, notice that

$$c_i^F(0) \leq \sum_{z_k<0} z_k^- c_k^F(0) = \sum_{z_k>0} z_k^+ c_k^F(0) \leq n z_{\max}^+ \max_k c_k^F(0).$$

Thus there is an index l such that $z_l > 0$ and $c_l^F(0) \geq \dfrac{c_i^F(0)}{n z_{\max}^+}$. Therefore

$$c_i^F(0)\,\frac{e^\alpha - 1}{n z_{\max}^+} \leq c_i^F(0)\,\frac{z_l(e^{\alpha z_l} - 1)}{n z_{\max}^+} \leq c_0^M$$

due to (14), hence if we start with $\eta < \eta_0$ then $e^{\alpha} < K$ by (13) with some $K > 0$ independent of $\lambda \in [0,1]$. Consequently,

$$c_i^M(0) = c_i^F(0)e^{\alpha z_i} \geq c_i^F(0)K^{-\bar{z}_{\max}} \geq \frac{\rho e^{-a^F\delta_F}}{2n(1+\bar{z}_{\max})}K^{-\bar{z}_{\max}}.$$

Since $\beta \geq 0$, this finally implies

$$\eta \geq c_i^P \geq c_i^M(\delta_M) \geq \frac{\rho e^{-a^F\delta_F}e^{-a^M\delta_M}}{2n(1+\bar{z}_{\max})}K^{-\bar{z}_{\max}} - \eta\frac{b^M}{a^M} \quad \text{for all } 0 < \eta < \eta_0,$$

a contradiction for sufficiently small $\eta > 0$.

Therefore the claim holds, hence

$$d(I - G, \Omega, 0) = d(I - H(\cdot,1), \Omega, 0) = d(I - H(\cdot,0), \Omega, 0).$$

The case $\lambda = 0$ corresponds to $D_i^j = 1$, $v^j = v^P$ and $c_0^M = 0$, where the solution is given by

$$\mathbf{c}^F \equiv \mathbf{c}^P,\ \mathbf{c}^M \equiv \mathbf{c}^P,\ \mathbf{c}^R = \mathbf{c}^P\ (= \frac{A^M\dot{V}^f}{A^F\dot{V}^P + A^M\dot{V}^R}\mathbf{c}^f).$$

This yields $H(\mathbf{c}^P, 0) = \mathbf{c}^P/\sigma$, hence (eventually after adjustment of η)

$$d(I - H(\cdot,0), \Omega, 0) = d((1+\frac{1}{\sigma})I - \bar{\mathbf{c}}, \Omega, 0) = 1.$$

Consequently there is at least one fixed-point of G, i.e. a solution of the stationary problem.

□

Although uniqueness is to be expected from the physical viewpoint, this has not yet been proven mathematically.

4. The Instationary Problem.

Electroneutrality again allows for elimination of the electrical field which leads to a strongly coupled quasilinear parabolic system with nonlinear transmission and dynamical boundary conditions. Of course we now also assume inital conditions

$$\mathbf{c}^R(0) = \mathbf{c}_0^R, \quad \mathbf{c}^F(0,\cdot) = \mathbf{c}_0^F \text{ on } [-\delta_F, 0], \quad \mathbf{c}^M(0,\cdot) = \mathbf{c}_0^M \text{ on } [0,\delta_M], \quad \mathbf{c}^P(0) = \mathbf{c}_0^P. \quad (15)$$

Theorem 2. *Fix $p > 3/2$. Suppose that all initial values are strictly positive satisfying*

$$\mathbf{c}_0^F \in W_p^{2-2/p}([-\delta_F, 0]; \mathbb{R}^n), \quad \mathbf{c}_0^M \in W_p^{2-2/p}([0,\delta_M]; \mathbb{R}^n),$$

the electroneutrality conditions

$$\langle \mathbf{z}, \mathbf{c}_0^R\rangle = \langle \mathbf{z}, \mathbf{c}_0^P\rangle = 0, \quad \langle \mathbf{z}, \mathbf{c}_0^F\rangle = 0 \textit{ a.e. on } [-\delta_F, 0], \quad \langle \mathbf{z}, \mathbf{c}_0^M\rangle = c_0^M \textit{ a.e. on } [0,\delta_M]$$

as well as the compatibilty conditions corresponding to (4), (5) and (6).

Then there is a unique solution $(\mathbf{c}^R, \mathbf{c}^F, \mathbf{c}^M, \mathbf{c}^P)$ *of the instationary problem (1), (3), (4), (5), (6) on a time interval* $[0,T]$ *for some* $T > 0$. *The solution is continuous with values in the phase space*

$$\mathbb{R}^n \times W_p^{2-2/p}([-\delta_F, 0]; \mathbb{R}^n) \times W_p^{2-2/p}([0, \delta_M]; \mathbb{R}^n) \times \mathbb{R}^n,$$

stays electroneutral and depends continuously on the data. The differential equations are satisfied in the strong L^p*-sense and the boundary as well as transmission conditions hold pointwise.*

The proof of this result is based on L^p-maximal regularity (cf. [4]) of an appropriately linearized system and will be given in a forthcoming paper.

Acknowledgement. The subject of this paper was brought to our attention by D. Jakobs and H.-J. Warnecke, University of Paderborn. We appreciate many helpful discussions and are grateful for the continuing cooperation.

References

[1] H. Amann, M. Renardy: Reaction-Diffusion problems in electrolysis. NoDEA **1**, 91-117 (1994).

[2] Y.S. Choi, R. Lui: Multi-dimensional electrochemistry model. Arch. Rational Mech. Anal. **130**, 315-342 (1995).

[3] K. Deimling: *Nonlinear Functional Analysis.* Springer 1985.

[4] R. Denk, M. Hieber, J. Prüss: $\mathcal{R}$-Boundedness, Fourier Multipliers and Problems of Elliptic and Parabolic Type. Reports of the Institute of Analysis, Univ. Halle-Wittenberg 2001.

[5] D. Jakobs: Stofftransport durch Nanofiltrationsmembranen unter Berücksichtigung von Biofilmen. PhD-Dissertation Univ. Paderborn 2001.

[6] M. Mulder: *Basic Principles of Membrane Technology*, 2$^{\text{nd}}$ edition. Kluwer 1997.

[7] J.S. Newman: *Electrochemical Systems*, 2$^{\text{nd}}$ edition. Prentice Hall 1991.

[8] S.I. Pohozaev: On the reaction-diffusion electrolysis nonlinear elliptic equations. Lect. Notes Pure Appl. Math. **194**, 255-288 (1998).

[9] J. Wiedmann: An electrolysis model and its solutions. PhD-Dissertation Univ. Zürich 1997.