A study of concentration and potential in a porous electrode

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Abstract

We find explicit expressions for the concentration and potential as functions of time during discharge in three different models of a cell with a porous metal hydride electrode. The effect of convection is studied and estimates of the convergence rate to the steady state are given. An example of an electric-vehicle battery application is presented.

Keywords: Porous electrode; Discharge; Metal hydride electrodes

1. Introduction

Porous metal hydride electrodes are nowadays widely used in electrochemical cells. A battery with a metal hydride electrode has high energy density and for instance in an electric-vehicle application one of the greatest advantages of metal hydride batteries is the low weight compared to the traditional lead/acid battery. See Ref. [1] for an overview of metal hydride electrodes.

A typical metal hydride electrode consists of spherical metal hydride particles imbedded in a conducting material resulting in a porous structure. When the electrode is immersed in the electrolyte the void volume is filled. The operation of a metal hydride electrode in a battery is based on two reactions. The reaction

$$MH_x \rightarrow xM - H_{ads}$$

is a dehydridization reaction, where hydrogen is released from the hydride phase forming adsorbed hydrogen atoms. Current is generated in the electrochemical reaction

$$xM - H_{ads} + xOH^- \rightarrow xe^- + xH_2O + xM$$
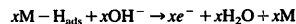
where the adsorbed hydrogen reacts with hydroxide ions producing electrons and water. Combining these two we get the total reaction

$$MH_x + xOH^- \rightarrow xe^- + xH_2O + xM$$
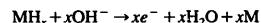
Although metal hydride alloys and electrodes have recently been widely studied in the literature there are only a few models concerning their electrochemical behavior. In Ref.

[2] a complete cell with a flat plate hydrogen electrode is theoretically analyzed. A model with a thick metal hydride electrode is presented in Refs. [3,4] but this model, however, ignores the diffusion and convection in the electrolyte and constant concentration and steady state throughout the cell is assumed. In reality these assumptions are not necessarily valid. For example, the porous material in the cell prevents spontaneous mixing of the electrolyte which means that concentration variations can exist even in the steady state. Since the concentration is one of the crucial factors affecting the corrosion and the life time of a cell it is important to know the concentration distribution inside the cell. To increase the life time of electrodes we want to find methods to prevent too high concentrations. One way to achieve this is to employ convection through the cell. Convection can of course be produced externally with different arrangements, but a much more interesting case, however, is the natural convection inside the cell caused, for instance, by temperature gradients.

In this paper we consider mass transfer in the presence of a porous metal hydride electrode and convection parallel to the motion of ions in the cell. Electrode phenomena and interfacial effects such as electric double layers and surface overpotential are neglected.

Three different electrochemical systems are described. In all these systems a porous thick metal hydride electrode is placed next to a thin counter electrode. The rest of the system is filled with passive medium having the same porosity and tortuosity as the metal hydride. The three cases are: (i) closed cell with no convection; (ii) closed loop, and (iii) an infinite tube. In the last two cases we include convection.

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In each case, we derive explicit expressions for the concentration and potential as functions of time as well as in the steady state. The convergence rate to the steady state is estimated and the effect of convection is investigated.

In a forthcoming article we include reaction dynamics of the metal hydride electrode with hydrogen diffusion in metal hydride particles and optimize the structure of the porous electrode.

2. Methods and models

2.1. Preliminaries

We use the Nernst–Planck equation [5] to describe the flux density j_i of an ion species i. In the presence of a porous medium with porosity ϵ the equation takes the form

$$j_i = - \epsilon^{1.5} D_i^{\text{free}} \nabla c_i - \frac{\epsilon^{1.5} \sigma_i^{\text{free}}}{F} \nabla \phi + \boldsymbol{v}_i c_i \qquad (1)$$

where c_i is the concentration of the ion species i in the solution phase, $\boldsymbol{v}_i$ is the superficial bulk fluid velocity and ϕ is the potential of the electric field. D_i^{free} is the diffusion coefficient and σ_i^{free} is the signed ionic conductivity of the species i in the absence of the porous medium. We use the factor $\epsilon^{1.5}$ to compensate the effects of porosity and tortuosity as in Ref. [6]. The terms on the right-hand side of Eq. (1) model the contributions of diffusion, migration and convection, respectively. The migration term is often presented as

$$j_i^{\text{migration}} = - z_i F \epsilon^{1.5} u_i^{\text{free}} c_i \nabla \phi \qquad (2)$$

where $z_i F$ is the charge per mole and u_i^{free} is the mobility of the species i without the porous medium. Both forms of the migration term will be used later.

To keep notation short we introduce

$$D_i = \epsilon^{1.5} D_i^{\text{free}}$$

$$\sigma_i = \epsilon^{1.5} \sigma_i^{\text{free}}$$

and

$$u_i = \epsilon^{1.5} u_i^{\text{free}}$$

Strictly speaking, the Nernst–Planck equations should be used to describe mass transfer only in dilute solutions but we apply them due to their simplicity and the fact that they are widely used in electrochemical literature.

We consider a binary electrolyte of two species of charged ions with opposite unit charges and nonionized solvent. We make the customary electroneutrality assumption and denote the common concentration by c. The superscripts '+' and '−' of the diffusion coefficients, ionic conductivities, mobilities and convection velocities refer to positive and negative ions, respectively. From now on we use a convention where both ionic conductivities are positive. The mass balance equations can then be written as

$$\epsilon c_t = - \nabla \cdot \left(- D^- \nabla c + \frac{\sigma^-}{F} \nabla \phi + \boldsymbol{v}^- c \right) + R^- \qquad (3)$$

$$\epsilon c_t = - \nabla \cdot \left(- D^+ \nabla c - \frac{\sigma^+}{F} \nabla \phi + \boldsymbol{v}^+ c \right) + R^+ \qquad (4)$$

where the inhomogeneous terms R^+ and R^- are production rates per unit volume of positive and negative ions, respectively. Generally, the diffusion coefficients, ionic conductivities, mobilities as well as convection velocities depend on concentration.

Our aim is to use analytical methods as long as possible and thus we simplify Eqs. (3) and (4) considerably. First of all, we assume that the concentration and electric potential vary only in the axial direction of the cell. To keep the treatment simple we use the velocity of the solvent as the convection velocity for all ion species. This is a good approximation for dilute solutions. Furthermore, we ignore the viscous forces and assume that the solvent velocity is axial and constant throughout the cell. The (scalar) solvent velocity is denoted by v. Hence Eqs. (1)–(4) reduce to a one-dimensional form. By assuming that the porosity is constant throughout the cell we avoid discontinuities in the coefficients of our mass balance equations. The effect of axial dispersion on diffusion coefficients has been neglected. Finally, we assume that the cell is discharged with constant current and that all the coefficients and the initial state are constant.

We apply two different models for the migration term. When the concentration variations in the cell are small or a simple model is desired we use

$$j_{\pm}^{\text{migration}} = \mp \frac{\sigma^{\pm}}{F} \phi_x \qquad (5)$$

where the ionic conductivities $\sigma^{\pm}$ are constants. If the concentration is expected to vary significantly it is better to define

$$j_{\pm}^{\text{migration}} = \mp F u^{\pm} c \phi_x \qquad (6)$$

where the mobilities $u^{\pm}$ are constant but there is a linear dependence on concentration.

When modelling electrochemical cells it is customary to assume that there are concentration variations only in thin boundary layers next to the electrodes and that the bulk of the electrolyte remains in the constant initial state. In our application, however, porous medium fills the whole cell and thus we assume that there are neither spontaneous mixing nor other processes that would even out concentration differences in the electrolyte. Hence we apply Eqs. (3) and (4) throughout the cell, not only near the electrodes.

Usually the inhomogeneous terms R^+ and R^- arise from chemical reactions taking place in the electrolyte. Now there are no chemical reactions in the electrolyte itself but OH^- ions are produced at the counter electrode and destroyed on the surface of the porous metal hydride electrode. Thus we can use $R^+ = R^+_{\text{source}} - R^+_{\text{sink}}$ and $R^- = R^-_{\text{source}} - R^-_{\text{sink}}$ to model the electrodes as in Ref. [6].

Accordingly, the porous metal hydride electrode appears as a sink term for OH^- ions in Eq. (3) in all our three cases.

On the other hand, it is less conventional to use the same approach in describing the thin counter electrode with a source term instead of a boundary condition. This approach is very attractive due to its simplicity. We do not have to pay attention to directing the ions forming at the counter electrode to up or down stream. Instead, the ion flux from the counter electrode is controlled by diffusion, migration and convection in the same way as everywhere else in the cell.

Since the positive ions are passive and do not take part in reactions we have $R^+ = 0$ everywhere.

During discharge hydrogen is consumed according to the local reaction rate which varies throughout the electrode. The reaction rate depends, among other things, on the concentration and potential of the electrolyte, the potential of the metal hydride and the concentration of the hydrogen atoms on the surface of the metal hydride particles [4]. In optimizing the performance of the electrode one goal is to ensure that hydrogen is consumed uniformly. Otherwise some parts of the electrode would become passive before the total hydrogen storage is exhausted and thus the efficiency of the battery would decrease towards the end of the discharge.

Thus we assume that all the OH⁻ ions that are produced on the counter electrode react on the metal hydride electrode and that this reaction rate is uniform throughout the metal hydride, corresponding to the optimal operation of the electrode.

Hence, if the counter electrode is located at $x = x_1$ and the metal hydride electrode occupies the region between the points $x = x_1$ and $x = x_r$, we set

$$R_{\text{sink}}^- = J^- \frac{\chi_{(x_1, x_r]}}{x_r - x_1}$$

where

$$\chi_D(x) = \begin{cases} 1, & \text{if } x \in D \\ 0, & \text{otherwise} \end{cases}$$

is the characteristic function of the interval D and J^- is the current density at the counter electrode expressed in flux density units mol/m² s. Then

$$\int_{-\infty}^{\infty} R_{\text{sink}}^-(\xi) \, d\xi = J^-$$

as desired. In the closed cell case the counter electrode is modelled as a boundary condition

$$j^-|_{x=x_1} = J^-$$

so that $R_{\text{source}}^- = 0$ but in the other two cases we set

$$R_{\text{source}^-} = J^- \delta_{x_1}$$

where $\delta_{x_1}(x) = \delta(x - x_1)$ is a Dirac delta functional centered at $x = x_1$. That is, the counter electrode is described as a point-like source of OH⁻ ions.

In the following sections we frequently use the Heaviside step function h defined by

$$h(x) = \begin{cases} 0, & \text{if } x \le 0 \\ 1, & \text{if } x > 0 \end{cases}$$

and abbreviate $h_y(x) = h(x - y)$.

Note that according to our assumptions the ratio of the ionic conductivities of positive and negative ions is constant. Then the potential gradient can be eliminated from Eqs. (3) and (4) and the concentration depends only on the ratio of the migration terms but not on their explicit form.

In all models presented below the negative ions move from left to right in the metal hydride electrode so that the current is in the opposite direction.

2.2. Closed cell without convection

We consider a cell with a porous metal hydride electrode filling the region $(0, l]$ and a thin counter electrode placed at $x = 0$, see Fig. 1. We assume that there is no flow through the boundaries at $x = 0$ and $x = l$ and that there is no convection in the cell so that only diffusion and migration contribute to the mass transport.

Then the concentration and potential satisfy the equations

$$\frac{\partial}{\partial t} \epsilon c = -\frac{\partial}{\partial x}\left(-D^- c_x + \frac{\sigma^-}{F}\phi_x \right) - \frac{J^-}{l} \tag{7}$$

$$\frac{\partial}{\partial t} \epsilon c = -\frac{\partial}{\partial x}\left(-D^+ c_x - \frac{\sigma^+}{F}\phi_x \right) \tag{8}$$

for $0 < x < l$, $t > 0$ with the boundary conditions

$$\left(-D^- c_x + \frac{\sigma^-}{F}\phi_x \right)\bigg|_{x=0} = J^- \tag{9}$$

$$\left(-D^+ c_x - \frac{\sigma^+}{F}\phi_x \right)\bigg|_{x=0} = 0 \tag{10}$$

$$\left(-D^- c_x + \frac{\sigma^-}{F}\phi_x \right)\bigg|_{x=l} = 0 \tag{11}$$

$$\left(-D^+ c_x - \frac{\sigma^+}{F}\phi_x \right)\bigg|_{x=l} = 0 \tag{12}$$

that hold for all $t > 0$. The initial condition is

$$c(0, x) = c_0 \tag{13}$$

for $0 \le x \le l$.

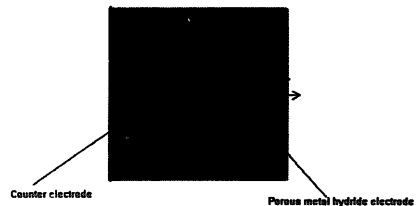Counter electrode   Porous metal hydride electrode

Fig. 1. Closed cell.

Note that according to the boundary conditions (9) and (11) and the inhomogeneous sink term in Eq. (7) the current fed into the electrolyte at $x = 0$ is uniformly gathered by the porous metal hydride electrode on the interval $(0, l)$ so that the flux of the negative ions vanishes at $x = l$. On the other hand, the boundary conditions (10) and (12) and Eq. (8) are formulated so that the positive ions do not react on the electrodes.

For later use, we derive an equivalent set of boundary conditions by solving the Eqs. (9)–(12) for the concentration and potential gradients at the boundaries:

$$c_x|_{x=0} = -\frac{\sigma^+ J^-}{D^+ \sigma^- + D^- \sigma^+} \tag{14}$$

$$c_x|_{x=l} = 0 \tag{15}$$

$$\phi_x|_{x=0} = \frac{F D^+ J^-}{D^+ \sigma^- + D^- \sigma^+} \tag{16}$$

$$\phi_x|_{x=l} = 0 \tag{17}$$

From Eqs.(7) and (8) and the boundary conditions (14) and (15) we obtain after some manipulations

$$\epsilon c_t = D c_{xx} - \frac{t^+ J^-}{l} \tag{18}$$

with

$$c_x|_{x=0} = -\frac{t^+ J^-}{D} \tag{19}$$

$$c_x|_{x=l} = 0 \tag{20}$$

where

$$D = \frac{D^- \sigma^+ + D^+ \sigma^-}{\sigma^+ + \sigma^-}$$

is the integral diffusion coefficient and

$$t^+ = \frac{\sigma^+}{\sigma^+ + \sigma^-}$$

is the transference number of positive ions.

In order to use the separation of variables method [7] for solving the system Eqs. (18)–(20) with the initial condition (13) we make a change of the unknown. We define

$$u = c - \frac{t^+ J^-}{2lD} x^2 + \frac{t^+ J^-}{D} x$$

Then the original problem transforms to the homogeneous diffusion equation

$$\epsilon u_t = D u_{xx} \tag{21}$$

with the homogeneous boundary conditions

$$u_x|_{x=0} = u_x|_{x=l} = 0 \tag{22}$$

and the initial condition

$$u(0, x) = c_0 - \frac{t^+ J^-}{2lD} x^2 + \frac{t^+ J^-}{D} x \tag{23}$$

The transformed problem (21)–(23) is easily solved and the solution of the original problem is then given by

$$c(t, x) = c_0 + \frac{t^+ J^- l}{D} \left[\frac{1}{3} - \frac{x}{l} + \frac{1}{2} \frac{x^2}{l^2} - 2 \sum_{n=1}^{\infty} \frac{1}{n^2 \pi^2} \exp\left(-\frac{n^2 \pi^2 D}{l^2 \epsilon} t \right) \cos\left(\frac{n\pi}{l} x \right) \right] \tag{24}$$

Here, as well as in the two other cases, the partial differential equation can alternatively be solved with Laplace transforms but the solution is again expressed in terms of a series.

With the constant ionic conductivities (5), by subtracting Eq. (8) from Eq. (7) and rearranging the terms, we obtain

$$\frac{\partial}{\partial x}\left(\frac{\sigma^- + \sigma^+}{F} \phi_x \right) = (D^- - D^+) c_{xx} - \frac{J^-}{l} \tag{25}$$

Then, integrating Eq. (25) twice with respect to x and using the boundary conditions (14)–(17) yields

$$\phi(t, x) = \frac{F}{\sigma^- + \sigma^+} \left[(D^- - D^+) c(t, x) + J^- \left(x - \frac{x^2}{2l} \right) \right] \tag{26}$$

Similarly, using the linear concentration dependence (6) for the ionic conductivities leads to

$$\phi(t, x) = \frac{1}{F(u^- + u^+)} \left[(D^- - D^+) \ln \frac{c(t, x)}{c(t, 0)} + \frac{J^-}{l} \int_0^x \frac{l - \xi}{c(t, \xi)} d\xi \right] \tag{27}$$

From Eq. (24) it is easy to see that the steady state solution defined by $C(x) = \lim_{t \to \infty} c(t, x)$ is

$$C(x) = c_0 + \frac{t^+ J^- l}{D} \left(\frac{1}{3} - \frac{x}{l} + \frac{1}{2} \frac{x^2}{l^2} \right) \tag{28}$$

and that for all $x \in [0, l]$

$$|c(t, x) - C(x)| \leq \left(\frac{2 t^+ J^- l}{D \pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \right) \exp\left(-\frac{\pi^2 D}{l^2 \epsilon} t \right)$$

$$\leq \frac{4 t^+ J^- l}{D \pi^2} \exp\left(-\frac{\pi^2 D}{l^2 \epsilon} t \right)$$

That is, the concentration converges uniformly to the steady state with exponential rate. Note that shortening the electrode, i.e. making l smaller, makes the convergence faster.

Expressions for the steady state potentials can be derived by substituting the steady state concentration given by Eq. (28) into Eqs. (26) and (27).

2.3. Circular cell with convection

The reason for studying a circular cell is that we wanted to find a simple model compatible with forced or natural convection through the electrodes. The opposite ends of a closed
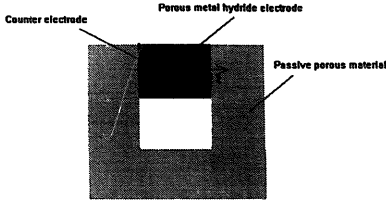
Fig. 2. Circular cell.

cell like the one described previously are connected with a tube making electrolyte circulation through the electrodes possible. Below we present an idealization of this arrangement.

We consider an imaginary electrochemical system consisting of a thin tube in which there are two electrodes (Fig. 2). The metal hydride electrode occupies the interval $(x_1, x_2]$ and the infinitely thin counter electrode is placed at $x = x_1$. The ends of the tube are connected and it forms a closed loop. Thus there are two routes for the current to pass from one electrode to the other.

The mathematical model is as follows. The concentration c and potential ϕ satisfy the equations

$$\epsilon c_t = -\frac{\partial}{\partial x}\left(-D^- c_x + \frac{\sigma^-}{F}\phi_x + cv\right) + J^-\left(\delta_{x_1} - \frac{\chi_{(x_1, x_2]}}{x_2 - x_1}\right) \tag{29}$$

$$\epsilon c_t = -\frac{\partial}{\partial x}\left(-D^+ c_x - \frac{\sigma^+}{F}\phi_x + cv\right) \tag{30}$$

for $0 < x \le L$ and $t > 0$.

Due to the circular nature of the cell the boundary conditions are periodic:

$$c(t, 0) = c(t, L) \tag{31}$$

$$\phi_x(t, 0) = \phi_x(t, L) \tag{32}$$

and

$$j^-(t, 0) = j^-(t, L), \quad j^+(t, 0) = j^+(t, L) \tag{33}$$

where

$$j^- = -D^- c_x + \frac{\sigma^-}{F}\phi_x + cv$$

and

$$j^+ = -D^+ c_x - \frac{\sigma^+}{F}\phi_x + cv$$

In other words, we require that the concentration, electric field and flux density are periodic. It follows from Eqs.(31)–(33) that the concentration derivative is periodic as well

$$c_x(t, 0) = c_x(t, L) \tag{34}$$

Finally we set an initial condition

$$c(0, x) = c_0, \quad 0 \le x < L \tag{35}$$

Eliminating the migration terms from Eqs. (29) and (30) leads to an equation for the concentration

$$\epsilon c_t = D c_{xx} - v c_x + t^+ J^-\left(\delta_{x_1} - \frac{\chi_{(x_1, x_2]}}{x_2 - x_1}\right) \tag{36}$$

The periodic boundary conditions (31) and (34) encourage us to use a Fourier series method (see Ref. [7]) to solve the problem involving Eqs.(36), (31), (34) and (35). We first solve the problem with zero initial condition and then add c_0 to the solution to find the solution to the original problem.

We define

$$C_n(t) = \frac{1}{L}\int_0^L c(t, \xi) \exp\left(-i\frac{2n\pi}{L}\xi\right) d\xi$$

where n is an integer. Then Eq. (36) transforms to

$$\epsilon C_n'(t) = -\left(D\frac{4n^2\pi^2}{L^2} + v c i\frac{2n\pi}{L}\right)C_n(t)$$

$$+ t^+ J^-\left\{\frac{1}{L}\exp\left(-i\frac{2n\pi}{L}x_1\right)\right.$$

$$\left. - \frac{i}{2n\pi(x_2 - x_1)}\left[\exp\left(-i\frac{2n\pi}{L}x_2\right) - \exp\left(-i\frac{2n\pi}{L}x_1\right)\right]\right\}$$

whose solution with the transformed initial condition $C_n(0) = 0$ is

$$C_n(t) = t^+ J^-\left(D\frac{4n^2\pi^2}{L^2} + vi\frac{2n\pi}{L}\right)^{-1}\left\{\frac{1}{L}\exp\left(-i\frac{2n\pi}{L}x_1\right)\right.$$

$$\left. - \frac{i}{2n\pi(x_2 - x_1)}\left[\exp\left(-i\frac{2n\pi}{L}x_2\right) - \exp\left(-i\frac{2n\pi}{L}x_1\right)\right]\right\}$$

$$\left\{1 - \exp\left[-\left(\frac{4Dn^2\pi^2}{L^2} + i\frac{2vn\pi}{L}\right)\frac{t}{\epsilon}\right]\right\}$$

for $n \ne 0$.

We now determine C_0. It follows from Eq. (30) and the boundary condition (33) that the mass is conserved

$$\frac{d}{dt}\int_0^L c(t, \xi) d\xi = 0$$

With the temporary zero initial condition this means that

$$\int_0^L c(t, \xi) d\xi = 0$$

for $t \ge 0$. Thus $C_0(t) = 0$.

Then the solution to Eq. (36) together with the boundary and initial conditions is given by a doubly infinite series

$$c(t, x) = c_0 + \sum_{n=-\infty}^{\infty} C_n(t) \exp\left(i\frac{2n\pi}{L}x\right)$$

Since the concentration is a real function we can also express it as:

$$c(t, x) = c_0 + \sum_{n=1}^{\infty} \left[a_n(t) \cos\left(\frac{2n\pi}{L}x\right) + b_n(t) \sin\left(\frac{2n\pi}{L}x\right) \right]$$

(37)

where

$$a_n(t) = 2 \operatorname{Re} C_n(t)$$

$$= \frac{t^+ J^- L^2}{4D^2 n^3 \pi^3 + v^2 L^2 n\pi}$$

$$\times \left[1 - \exp\left(-\frac{4Dn^2\pi^2}{L^2}\frac{t}{\epsilon}\right) \cos\frac{2n\pi}{L}\frac{t}{\epsilon} \right]$$

$$\times \left\{ 2Dn\pi \left[\frac{1}{L}\cos\frac{2n\pi}{L}x_1 - \frac{1}{2n\pi(x_2 - x_1)} \right. \right.$$

$$\times \left(\sin\frac{2n\pi}{L}x_2 - \sin\frac{2n\pi}{L}x_1 \right) \right] - vL\left[\frac{1}{L}\sin\frac{2n\pi}{L}x_1 \right.$$

$$\left. + \frac{1}{2n\pi(x_2 - x_1)} \left(\cos\frac{2n\pi}{L}x_2 - \cos\frac{2n\pi}{L}x_1 \right) \right] \right\}$$

$$+ \exp\left(-\frac{4Dn^2\pi^2}{L^2}\frac{t}{\epsilon}\right) \sin\frac{v2n\pi}{L}\frac{t}{\epsilon} \left\{ 2Dn\pi \right.$$

$$\times \left[\frac{1}{L}\sin\frac{2n\pi}{L}x_1 + \frac{1}{2n\pi(x_2 - x_1)} \left(\cos\frac{2n\pi}{L}x_2 \right. \right.$$

$$\left. - \cos\frac{2n\pi}{L}x_1 \right) \right] + vL\left[\frac{1}{L}\cos\frac{2n\pi}{L}x_1 - \frac{1}{2n\pi(x_2 - x_1)} \right.$$

$$\left. \left. \times \left(\sin\frac{2n\pi}{L}x_2 - \sin\frac{2n\pi}{L}x_1 \right) \right] \right\} \right)$$

(38)

and

$$b_n(t) = -2 \operatorname{Im} C_n(t)$$

$$= -\frac{t^+ J^- L^2}{4D^2 n^3 \pi^3 + v^2 L^2 n\pi}$$

$$\times \left[\exp\left(-\frac{4Dn^2\pi^2}{L^2}\frac{t}{\epsilon}\right) \sin\frac{v2n\pi}{L}\frac{t}{\epsilon} \right.$$

$$\times \left\{ 2Dn\pi \left[\frac{1}{L}\cos\frac{2n\pi}{L}x_1 - \frac{1}{2n\pi(x_2 - x_1)} \right. \right.$$

$$\times \left(\sin\frac{2n\pi}{L}x_2 - \sin\frac{2n\pi}{L}x_1 \right) \right] - vL\left[\frac{1}{L}\sin\frac{2n\pi}{L}x_1 \right.$$

$$\left. + \frac{1}{2n\pi(x_2 - x_1)} \left(\cos\frac{2n\pi}{L}x_2 - \cos\frac{2n\pi}{L}x_1 \right) \right] \right\}$$

$$\left. - \left[1 - \exp\left(-\frac{4Dn^2\pi^2}{L^2}\frac{t}{\epsilon}\right) \cos\frac{v2n\pi}{L}\frac{t}{\epsilon} \right] \right.$$

$$\times \left\{ 2Dn\pi \left[\frac{1}{L}\sin\frac{2n\pi}{L}x_1 + \frac{1}{2n\pi(x_2 - x_1)} \right. \right.$$

$$\times \left(\cos\frac{2n\pi}{L}x_2 - \cos\frac{2n\pi}{L}x_1 \right) \right] + vL\left[\frac{1}{L}\cos\frac{2n\pi}{L}x_1 \right.$$

$$\left. - \frac{1}{2n\pi(x_2 - x_1)} \times \left(\sin\frac{2n\pi}{L}x_2 - \sin\frac{2n\pi}{L}x_1 \right) \right] \right\} \right]$$

(39)

To find an expression for the potential when the ionic conductivities are constant (model (5)) we subtract Eq. (29) from Eq. (30) to eliminate the time derivatives and convection terms and solve for ϕ_{xx}. This yields

$$\phi_{xx} = \frac{F}{\sigma^+ + \sigma^-} \left[(D^- - D^+)c_{xx} + J^- \left(\delta_{x_1} - \frac{\chi_{(x_1, x_2)}}{x_2 - x_1} \right) \right]$$

Integrating the previous equation with respect to x leads to

$$\phi_x(t, x) = \frac{F}{\sigma^+ + \sigma^-} \left[(D^- - D^+)c_x(t, x) \right.$$

$$\left. + J^- \frac{x_2 - x}{x_2 - x_1} \chi_{(x_1, x_2)}(x) + A(t) \right]$$

where A is an arbitrary function of t. Note that this expression is periodic for every choice of the integration constant A. To determine the potential we must thus find an extra condition for ϕ. It is very natural to require that that the potential itself is periodic too

$$\phi(t, 0) = \phi(t, L)$$

Then

$$A(t) = -\frac{J^-}{2L}(x_2 - x_1)$$

for all $t > 0$. With this choice we get, after an additional integration,

$$\phi(t, x) = \frac{F}{\sigma^+ + \sigma^-} \left\{ (D^- - D^+)c(t, x) \right.$$

$$+ J^- \left[\frac{2x_2(x - x_1) - (x^2 - x_1^2)}{2(x_2 - x_1)} \chi_{(x_1, x_2)}(x) \right.$$

$$\left. \left. + \frac{1}{2}(x_2 - x_1)h_{x_2}(x) - \frac{1}{2L}(x_2 - x_1)x \right] \right\}$$

(40)

When the ionic conductivities depend linearly on concentration (model (6)) the potential can be expressed as

$$\phi(t, x) = \frac{1}{F(u^+ + u^-)} \left\{ (D^- - D^+) \ln c(t, x) \right.$$

$$+ J^- \left[\int_0^x \frac{x_2 - \xi}{c(t, \xi)(x_2 - x_1)} \chi_{[x_1, x_2]}(\xi) \, d\xi \right.$$

$$\left. \left. - \frac{\int_{x_1}^{x_2} \frac{x_2 - \xi}{c(t, \xi)(x_2 - x_1)} d\xi}{\int_0^L \frac{d\xi}{c(t, \xi)}} \int_0^x \frac{d\xi}{c(t, \xi)} \right] \right\} \quad (41)$$

From the series representation (37)–(39) it is easy to see that there is a steady state solution $C(x) = \lim_{t \to \infty} c(t, x)$ given by

$$c(t, x) = c_0 + \sum_{n=1}^{\infty} \left[(a_n(\infty) \cos\frac{2n\pi}{L}x + b_n(\infty) \sin\frac{2n\pi}{L}x \right] \quad (42)$$

where

$$a_n(\infty) = \lim_{t \to \infty} a_n(t)$$

$$= \frac{t^+ J^- L^2}{4D^2 n^3 \pi^3 + v^2 L^2 n\pi} \left\{ 2Dn\pi \left[\frac{1}{L} \cos\frac{2n\pi}{L}x_1 \right. \right.$$

$$\left. - \frac{1}{2n\pi(x_2 - x_1)} \left(\sin\frac{2n\pi}{L}x_2 - \sin\frac{2n\pi}{L}x_1 \right) \right]$$

$$- vL \left[\frac{1}{L} \sin\frac{2n\pi}{L}x_1 + \frac{1}{2n\pi(x_2 - x_1)} \right.$$

$$\left. \left. \times \left(\cos\frac{2n\pi}{L}x_2 - \cos\frac{2n\pi}{L}x_1 \right) \right] \right\}$$

and

$$b_n(\infty) = \lim_{t \to \infty} b_n(t)$$

$$= \frac{t^+ J^- L^2}{4D^2 n^3 \pi^3 + v^2 L^2 n\pi} \left\{ 2Dn.\pi \left[\frac{1}{L} \sin\frac{2n\pi}{L}x_1 \right. \right.$$

$$\left. + \frac{1}{2n\pi(x_2 - x_1)} \left(\cos\frac{2n\pi}{L}x_2 - \cos\frac{2n\pi}{L}x_1 \right) \right]$$

$$+ vL \left[\frac{1}{L} \cos\frac{2n\pi}{L}x_1 - \frac{1}{2n\pi(x_2 - x_1)} \right.$$

$$\left. \left. \times \left(\sin\frac{2n\pi}{L}x_2 - \sin\frac{2n\pi}{L}x_1 \right) \right] \right\}$$

Furthermore, for all $x \in [0, L]$:

$$|c(t, x) - C(x)| \leq K \exp\left(-\frac{4D\pi^2}{L^2} \frac{t}{\epsilon} \right)$$

where K is a constant. That is, the solution converges uniformly to the steady state with exponential rate. As before, decreasing the electrolyte volume, i.e. making L smaller, increases the convergence rate.

Expressions for the steady state potentials can be derived by substituting the steady state concentration given by Eq. (42) into Eqs. (40) and (41).

2.4. Infinite tube with convection

This is a limiting case of the circular cell. If we let the length of the loop tend to infinity we obtain a straight infinite tube as the limit. This case is of interest because it can be thought to model a cell connected to two big reservoirs of electrolyte. Contrary to the circular cell, there is no secondary route for the current. That is, all the current passes through the interval between the electrodes.

An infinite tube is filled with electrolyte, a porous metal hydride electrode occupies the region $(0, l]$ and a thin counter electrode is placed at $x = 0$ (Fig. 3). The concentration and potential satisfy the equations

$$\epsilon c_t = -\frac{\partial}{\partial x}\left(-D^- c_x + \frac{\sigma^-}{F}\phi_x + vc \right) + J^-\left(\delta_0 - \frac{\chi_{(0, l]}}{l} \right) \quad (43)$$

$$\epsilon c_t = -\frac{\partial}{\partial x}\left(-D^+ c_x - \frac{\sigma^+}{F}\phi_x + vc \right) \quad (44)$$

for $-\infty < x < \infty, t > 0$ with the initial condition:

$$c(0, x) = c_0 \quad (45)$$

for $-\infty < x < \infty$.

We use Fourier transformations (see Ref. [7]) to solve the problem involving Eqs. (43)–(45). Eliminating the migration terms from Eqs. (43) and (44) results in

$$\epsilon c_t = Dc_{xx} - vc_x + t^+ J^-\left(\delta_0 - \frac{\chi_{(0, l]}}{l} \right) \quad (46)$$

where D and t^+ are defined as before. The solution of Eq. (46) with Eq. (45) is given by

$$c(t, x) - c_0 = \int_0^{t/\epsilon} \int_{-\infty}^{\infty} \frac{t^+ J^-}{\sqrt{4\pi D(t/\epsilon - \tau)}}$$

$$\exp\left\{ -\frac{[x - \xi - v(t/\epsilon - \tau)]^2}{4D(t/\epsilon - \tau)} \right\} \left[\delta_0(\xi) \right.$$

$$\left. -\frac{1}{l}\chi_{(0, l]}(\xi) \right] d\xi \, d\tau = t^+ J^- \int_0^{t/\epsilon} \left\{ \frac{1}{\sqrt{4\pi D\tau}} \right.$$

$$\exp\left[-\frac{(x - v\tau)^2}{4D\tau} \right] - \frac{1}{2l}\left[\text{erf}\left(\frac{v\tau + l - x}{\sqrt{4D\tau}} \right) \right.$$

$$\left. \left. - \text{erf}\left(\frac{v\tau - x}{\sqrt{4D\tau}} \right) \right] \right\} d\tau \quad (47)$$

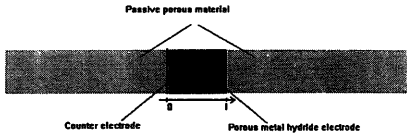where $\text{erf}(\cdot)$ is the error function.

Fig. 3. Infinite tube.

Let us now take a look at the potential when the ionic conductivities are constant (model (5)). We subtract Eq. (43) from Eq. (44) and solve for ϕ_{xx}. This yields

$$\phi_{xx} = \frac{F}{\sigma^- + \sigma^+}\left[(D^- - D^+)c_{xx} + J^-\left(\delta_0 - \frac{\chi_{(0,l)}}{l}\right)\right]$$

We integrate twice with respect to x and require that the electric field vanishes at infinity. As the result we get

$$\phi(t, x) = \frac{F}{\sigma^- + \sigma^+}\left\{(D^- - D^+)c(t, x)\right.$$
$$\left. + J^-\left[\left(x - \frac{1}{2l}x^2\right)\chi_{(0,l)}(x) + \frac{l}{2}h_l(x)\right]\right\} \qquad (48)$$

Suppose now that the ionic conductivity depends linearly on concentration (model (6)). Then the potential is given by

$$\phi(t, x) = \frac{1}{F(u^+ + u^-)}\left\{(D^- - D^+)\ln c(t, x)\right.$$
$$\left. + J^-\left[\int_0^x \frac{l-\xi}{lc(t, \xi)}\,d\xi\,\chi_{(0,l)}(x) + \int_0^l \frac{l-\xi}{lc(t, \xi)}\,d\xi\,h_l(x)\right]\right\}$$
$$(49)$$

Next we investigate the steady state. We let $C = \lim_{t\to\infty}c$ and define

$$f = \delta_0 - \frac{1}{l}\chi_{(0,l)}$$

so that

$$F(x) = \lim_{\delta\to 0^-}\int_\delta^x f(\xi)\,d\xi = \begin{cases}(l-x)/l & \text{if } x \in (0, l) \\ 0 & \text{if } x \notin [0, l]\end{cases}$$

Then, using partial integration, we find that

$$C(x) - c(t, x)$$

$$= t^+J^-\int_{t/\epsilon}^\infty\int_{-\infty}^\infty \frac{1}{\sqrt{4\pi D\tau}}\exp\left[-\frac{(x-\xi-v\tau)^2}{4D\tau}\right]f(\xi)\,d\xi\,d\tau$$

$$= t^+J^-\int_{t/\epsilon}^\infty \frac{1}{\sqrt{4\pi D\tau}}\left\{\exp\left[-\frac{(x-\xi-v\tau)^2}{4D\tau}\right]F(\xi)\,|_{\xi=-\infty}^{\xi=\infty}\right.$$

$$-\int_0^l \frac{2((x-\xi)-v\tau)}{4D\tau}\exp\left[-\frac{(x-\xi-v\tau)^2}{4D\tau}\right]F(\xi)\,d\xi\right\}d\tau$$

$$= -t^+J^-\int_{t/\epsilon}^\infty \frac{1}{\sqrt{4\pi D\tau}}\int_0^l \frac{2((x-\xi)-v\tau)}{4D\tau}$$

$$\times\exp\left[-\frac{(x-\xi-v\tau)^2}{4D\tau}\right]F(\xi)\,d\xi\,d\tau$$

$$= \frac{t^+J^-}{2D}\int_0^l F(\xi)\exp\left[\frac{(x-\xi)v}{D}\right]\left\{\text{erf}\left[\frac{(x-\xi)+v\tau}{2\sqrt{D\tau}}\right]\right\}\Big|_{\tau=t/\epsilon}^{\tau=\infty}d\xi$$

$$= \frac{t^+J^-}{2D}\int_0^l F(\xi)\exp\left[\frac{(x-\xi)v}{D}\right]$$

$$\times\left\{\text{sign}(v) - \text{erf}\left[\frac{(x-\xi)+vt/\epsilon}{2\sqrt{Dt/\epsilon}}\right]\right\}d\xi$$

From this it is easy to see that the solution converges pointwise to the steady state. Now assume that $x \in [0, l]$. If $v > 0$, then

$$|C(x) - c(t, x)| \leq \frac{t^+J^-}{2D}l\exp\left(\frac{lv}{D}\right)\left[1 - \text{erf}\left(\frac{-l+vt/\epsilon}{2\sqrt{Dt/\epsilon}}\right)\right]$$

For $v < 0$ we have

$$|C(x) - c(t, x)| \leq \frac{t^+J^-}{2D}l\exp\left(-\frac{lv}{D}\right)\left[1 + \text{erf}\left(\frac{l+vt/\epsilon}{2\sqrt{Dt/\epsilon}}\right)\right]$$

Finally, if $v = 0$ it follows that

$$|C(x) - c(t, x)| \leq \frac{t^+J^-}{2D}l\,\text{erf}\left(\frac{l}{2\sqrt{Dt/\epsilon}}\right)$$

Thus, the larger the value of $|v|$ the faster the rate of convergence.

It is clear from Eq. (47) that the steady state solution is given by

$$C(x) = c_0 + t^+J^-\int_0^\infty\left\{\frac{1}{\sqrt{4\pi D\tau}}\exp\left[-\frac{(x-v\tau)^2}{4D\tau}\right]\right.$$
$$\left. - \frac{1}{2l}\left[\text{erf}\left(\frac{v\tau+l-x}{\sqrt{4D\tau}}\right) - \text{erf}\left(\frac{v\tau-x}{\sqrt{4D\tau}}\right)\right]\right\}d\tau \qquad (50)$$

Expressions for the steady state potentials can be derived by substituting the steady state concentration given by Eq. (50) into Eqs. (48) and (49).

3. An application

3.1. Parameters

In all our examples KOH is used as the electrolyte solution. The initial concentration is chosen to be 5 M. The ionic

Table 1
Electrochemical data

Parameter	Value	Refs.
D^{free} (m^2/s)	3.23×10^{-9}	[8]
Λ^{free} (m^2/Ω equiv)	1.17×10^{-2}	[8]
t^+	0.22	[9]
D_+^{free} (m^2/s)	2.07×10^{-9}	
D_-^{free} (m^2/s)	7.34×10^{-9}	
σ_+^{free} ($1/\Omega$ m)	12.87	
σ_-^{free} ($1/\Omega$ m)	45.63	
u_+^{free} (m^2mol/J s)	2.76×10^{-13}	
u_-^{free} (m^2mol/J s)	9.80×10^{-13}	
F (C/equiv)	96500	

diffusion coefficients, conductivities and mobilities for 5 M KOH electrolyte are derived from the integral diffusion coefficient and the equivalent conductance using the transference numbers. The values for these parameters are given in Table 1.

The absolute value of the convection velocity $|v|$ varies between 0 and 10^{-5} m/s. The velocities used here can easily be shown to be reasonable and are in good consistency with even quite small temperature differences, 10 °C for instance, frequently occurring in electrochemical systems.

Next we discuss the parameters describing the cell, the porous electrode and operating conditions that are given in Table 2.

The cell parameters are chosen for electric-vehicle applications, for example. Then it is convenient to assume a discharge time of about 3 h and a discharge current density of 100 mA/cm² corresponding to a flux density of 0.01 mol/ m² s of OH⁻ ions and a capacity of 300 mAh/cm² for the electrode. For instance, with a much-studied metal hydride alloy MmNi$_{3.5}$Co$_{0.8}$Al$_{0.4}$Mn$_{0.3}$ [10,11] having the capacity of about 250–270 mAh/g this means that the surface density of the metal hydride alloy is 1.1–1.2 g/cm².

The thickness of the electrode and its porosity are related. It seems that the optimal value for the porosity is about 0.5. Then, if the electrode has 3 wt.% polytetrafluoroethylene (PTFE) and 1 wt.% carbon as the electrically conducting binder material it follows that the electrode should be 3 mm thick. The thickness of the electrode is thus relatively high but it has been chosen keeping in mind sintering fabrication methods with which high discharge rates even for thick electrodes can be achieved.

Table 2
Cell parameters

Parameter	Value
J^- (mol/m²s)	0.01
l (m)	0.003
L (m)	0.1
ϵ	0.5
x_1 (m)	0.001
x_2 (m)	0.004
c_0 (mol/l)	5

With the thickness of 3 mm the capacity of the electrode is 1 Ah/cm³. To balance this we can use an NiOOH electrode [12] or an oxygen electrode as the counter electrode, for example.

In the case of the circular cell the total length of the tube, L, is chosen to be large compared with the length of the metal hydride electrode, $l = x_2 - x_1$. In this way the secondary current outside the metal hydride electrode is negligible.

4. Results

Applying the previously introduced mathematical models with the parameter values given above we computed concentration and potential profiles in various situations. We emphasize that by potential we mean the potential in the electrolyte solution. Also, when using the phrases constant and linear ionic conductivities we refer to models (5) and (6), respectively. In all cases below, the concentration and potential profiles only within the porous electrode are shown, that is, we are not concerned with the concentration and potential outside the metal hydride electrode.

In Fig. 4 the time dependence of concentration with the closed cell model is presented. After the discharge time of 3000 s no change in the concentration profile can be observed so that an approximate steady state has been reached. In this section we use the phrase steady state in this sense. The difference between the maximum and minimum concentrations inside the metal hydride electrode increases with discharge time. At the steady state a difference of 2.8 M has developed. The corresponding potential distributions with constant and linear ionic conductivities are shown in Figs. 5 and 6, respectively. The potential difference between the ends of the metal hydride electrode decreases with discharge time. At the steady state the difference is 45 mV for the constant ionic conductivity model and 42 mV for the linear ionic conductivity model.

To examine the possibility to change the concentration distribution and especially concentration differences inside
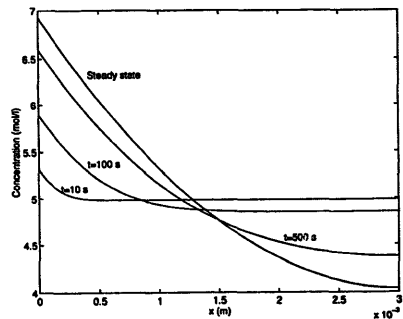

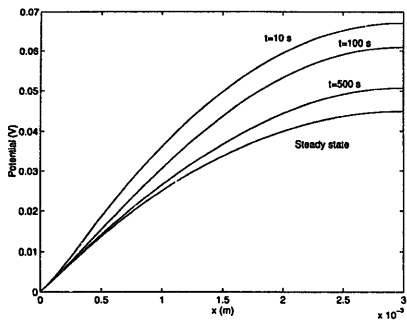Fig. 4. Concentration in the closed cell as a function of a time.

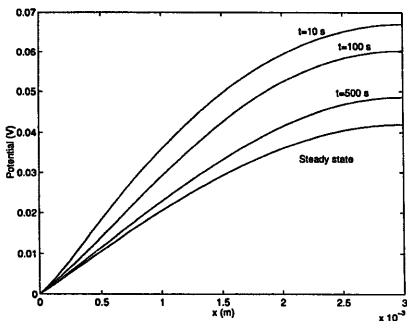Fig. 5. Potential in the cell as a function of time with constant ionic conductivities.

Fig. 6. Potential in the closed cell as a function of time with linear ionic conductivities.
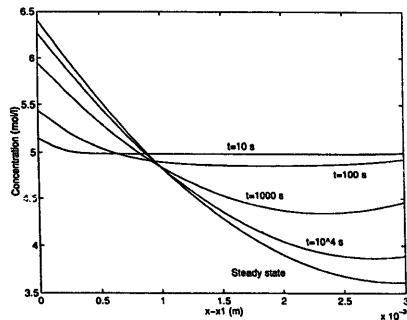

Fig. 7. Concentration in the circular cell as a function of time with no convection.

the electrode by using convection the two other cell models, i.e. circular cell and infinite tube, were studied. The physical validity and correspondence of these cases compared to the

closed cell were first investigated by calculating the concentration and potential distributions without convection. The concentration distributions for the circular cell and the infinite tube are presented in Figs. 7 and 8, respectively. Comparing these to Fig. 4 we see that the shapes of the concentration distributions are practically equal in each case and that the difference between the maximum and minimum concentrations has remained. On the other hand, the maxima and minima of the concentrations have become lower. This is due to the effect of the electrolyte reservoirs in the models. The main observation is however that the time needed to achieve a steady state is in both the circular cell and the infinite tube case beyond the assumed discharge time of 10 000 s and the times are now of the order of 5×10^5 and 5×10^6 s, respectively. This is an obvious consequence of the larger electrolyte volumes. The potential distributions in the circular cell and the infinite tube cases are not included because they are naturally almost equal to those of the closed cell case.

The effect of convection on the concentration distributions at the steady state is shown in Figs. 9 and 10 with different convection velocities. With low convection velocities of $\pm 10^{-7}$ m/s the differences between the maximum and minimum concentrations are practically the same as in the cases without convection, but the maxima and minima of the concentrations have become either lower or higher than without convection, depending on the direction of convection. With convection velocities of $\pm 10^{-5}$ m/s the shapes of the concentration profiles and differences between maximum and minimum concentrations are already markedly changed. When the convection is against the flow of negative ions the shape of concentration in the electrode is still continuously decreasing, but with the convection in the other direction the shape has been changed much more remarkably, that is, the minimum of the concentration has moved towards the counter electrode. In either case the difference between the maximum and minimum concentrations has decreased to 1 M from 2.8 M for the case without convection. With quite high convection velocities of $\pm 10^{-5}$ m/s the concentration profiles are
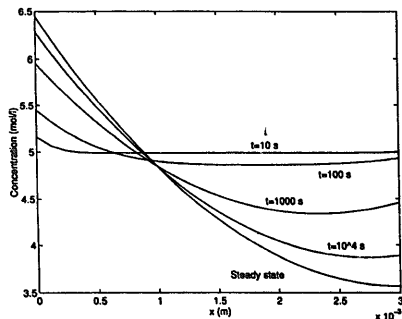

Fig. 8. Concentration in the infinite tube as a function of time with no convection.
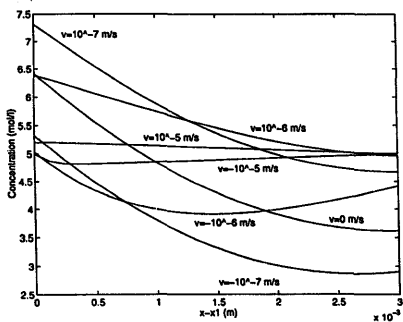
Fig. 9. Steady state concentration in the circular cell for different convection velocities.
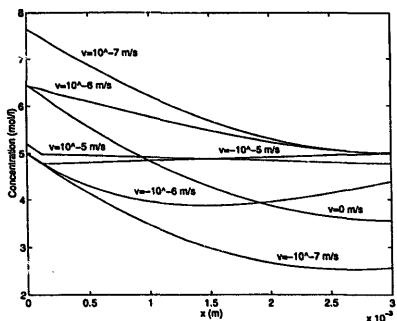

Fig. 10. Steady state concentration in the infinite tube for different convection velocities.

further flattened, so that the difference between the maxima and minima is only 0.2 M. Also the changes in the shape of the concentration profiles observed with the velocities of $\pm 10^{-6}$ m/s are further strengthened.

Note that in Fig. 10 the concentration at the down stream end of the metal hydride electrode in the infinite tube model is equal to 5 M, the initial concentration, when there is convection. This is due to the requirement of boundedness of solutions of the mass balance equations. In the circular cell case (Fig. 9) the down stream end concentration is pretty close to 5 M.

The potential distributions at the steady state with different convection velocities in the cases of constant and linear ionic conductivities are presented in Figs. 11 and 12 for the infinite tube model. The results for the circular cell are not shown because they are practically equal to those of the infinite tube.

In Fig. 11, where the constant ionic conductivity model was used, the potential distributions corresponding to low convection velocities of $\pm 10^{-7}$ m/s are very close to the potential distribution without convection. On the other hand,
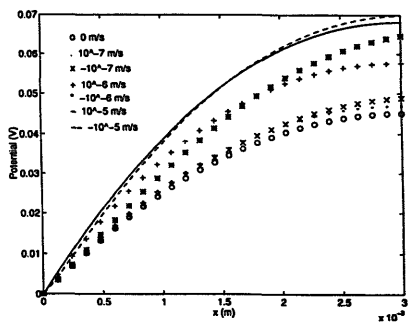

Fig. 11. Steady state potential in the infinite tube for different convection velocities with constant ionic conductivities.

with the linear model for ionic conductivities, shown in Fig. 12, these velocities cause noticeable differences. The potential difference between the electrode ends changes from 46 mV (no convection) to 37 mV (convection in the direction of negative ions) and to 71 mV (convection against the negative ions). This difference between Figs. 11 and 12 is easily explained by the concentration changes for velocities 0 and $\pm 10^{-7}$ m/s shown in Fig. 10 together with the linear ionic conductivity model.

From Fig. 11 it can be seen that the potential difference between the ends of the metal hydride electrode increases from 45 mV (no convection) to 58 or to 65 mV with the convection velocity of 10^{-6} m/s along with or against the negative ions, respectively, when constant ionic conductivities are assumed. With the linear ionic conductivities in Fig. 12 the potential difference between the ends of the metal hydride electrode has changed from 46 to 50 mV or 79 mV when the convection is 10^{-6} m/s along with or against the negative ions, respectively. Again the direction of the convection affects the potential more when the linear ionic conductivity model is used.
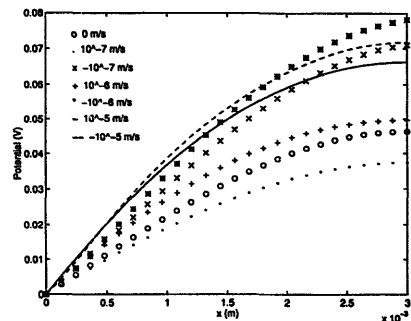

Fig. 12. Steady state potential in the infinite tube for different convection velocities with linear ionic conductivities.

With velocities of $\pm 10^{-5}$ m/s the effect of the direction of the convection is very much decreased especially in the case of constant ionic conductivities as can be seen from Fig. 11. The potential difference between the electrode ends has increased from 45 to about 69 mV regardless of the direction of convection. With the linear ionic conductivity model in Fig. 12 the potential difference has increased from 46 to about 70 mV.

5. Conclusions

From the above results it is obvious that the concentration distributions cannot be ignored in thick porous electrodes. Our examples show that quite remarkable concentration gradients are possible in such electrodes. It was also observed that the time needed to reach the steady state is much longer than what was expected. When electrolyte reservoirs were present, as in the models of circular cell and infinite tube in this presentation, this time was beyond the supposed discharge time of 3 h.

The concentration gradients can be affected by convection, if a suitable velocity is chosen. With high enough velocities (of the order of 10^{-5} m/s in our examples) the concentration profiles can be flattened almost totally, while with low velocities (of the order of 10^{-7} m/s in our examples) no effect on the difference between the maximum and minimum of concentrations is seen.

Even though flat concentration profiles can be thought to be advantageous because of lower concentration maxima and therefore reduced corrosion, flat profiles at the same time generally correspond to higher potential gradients inside the electrode. Since the electrolyte potential has a clear, and in some circumstances even very crucial, effect on corrosion rate, the steep potential profiles are also undesirable. Thus it seems that in trying to extend the life time of a cell optimizing the concentration and potential profiles is of great importance.

However, more attention should be paid to modelling the concentration dependence of the ionic conductivities. In this presentation only constant and linear models for the concentration dependence of ionic conductivities were used, because of the requirement of simplicity. Using these models, quite different results were obtained with lower velocities. With higher velocities the models gave almost identical results because the concentration differences in the electrode were very small.

6. List of symbols

c	concentration of negative and positive ions
C	steady state concentration of negative and positive ions
c_0	initial concentration of negative and positive ions
D	effective integral diffusion coefficient

D^{free}	integral diffusion coefficient
D^+	effective diffusion coefficient of positive ions
D^-	effective diffusion coefficient of negative ions
D_+^{free}	diffusion coefficient of positive ions
D_-^{free}	diffusion coefficient of negative ions
erf	error function
F	Faraday's constant
h_ξ	Heaviside step function with the step at $x = \xi$
j^+	scalar flux density of positive ions
j^-	scalar flux density of negative ions
J^-	discharge current in flux density units
l	length of the porous electrode
L	length of the cell
t	time
t^+	transference number of positive ions
u^+	effective mobility of positive ions
u^-	effective mobility of negative ions
u_+^{free}	mobility of positive ions
u_-^{free}	mobility of negative ions
v	scalar convection velocity of positive and negative ions
x	position
x_1	position of the left end of the porous electrode in the circular cell
x_2	position of the right end of the porous electrode in the circular cell

Greek symbols

χ_I	characteristic function of the interval I
δ_ξ	Dirac delta functional centered at $x = \xi$
ϵ	porosity of the electrode material
ϕ	electrostatic potential
Λ^{free}	equivalent conductance of the electrolyte
σ^+	effective ionic conductivity of positive ions
σ^-	effective ionic conductivity of negative ions
σ_+^{free}	ionic conductivity of positive ions
σ_-^{free}	ionic conductivity of negative ions

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