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Dynamical and stationary analysis of an electrolyte diode and comparison with experiments

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Abstract

Stationary and non-stationary behavior of an electrolyte diode system is studied. The system consists of a microcapillary connecting two reservoirs with a strong acid and strong base. If an external electric field is imposed on the capillary, diode like current-voltage characteristics is observed. A thin layer of electrolyte with extremely large pH gradient is formed in the closed regime of the diode. Transient behavior of the electrolyte diode is studied experimentally and numerically. Observed short-time overshoots of electric current in the current-voltage characteristics are explained based on numerical analysis of the reaction-transport processes in the capillary.

Keywords: electrolyte diode, electrophoresis, microchip, transients, mathematical modeling

1. Introduction

After connecting DC voltage to a microfluidic device consisting of two reservoirs (one contains a strong acid, HCl, and the other one strong base, KOH) separated by a permeation layer (Fig. 1), complex nonlinear behavior can be observed. Such microdevice is called *electrolyte diode* due to the similarity of the current-voltage characteristics with a semiconductor diode. When DC voltage is applied, two qualitatively different types of behavior of the electrolyte diode can be observed. If the positively charged electrode (anode) is placed in the KOH reservoir and the cathode is placed in the HCl reservoir, the system is in the open mode. The capillary then contains an electrolyte with high concentrations of potassium and chloride ions (KCl) and is characterized by a high level of electrolyte conductivity. If the electric field polarity is reversed, the electrolyte diode is in the closed mode. In the zone of the microcapillary where hydrogen and hydroxyl ions accumulate, water is formed. The narrow zone of water formation is characterized by a low value of electric conductivity. Hence the observed electric current response to the applied difference of electric potential is much lower than in the open mode. In this work, a positive difference of electric potential is related to the open mode and a negative difference to the closed mode. The difference is defined as a difference of electric potential between the alkaline and the acid reservoirs.

Studies on electrolyte diodes were reported, for example, by Hegedüs et al. (1995, 1996, 1998), Merkin et al. (2000), Lindner et al. (2002), and Šnita et al. (2001). The authors dealt with experimental realizations and/or numerical stationary analyses of such systems. Here, we compare experimental and numerical results of a dynamical analysis of the electrolyte diode carried out in a capillary microchip.

The interactions of ions with an externally applied electric field are important in many microfluidic applications: capillary electroseparation, electrokinetic dosing, sample addressing etc. The results obtained for the studied system can be relevant for more complex systems like microfluidic ionic gates and transistors.

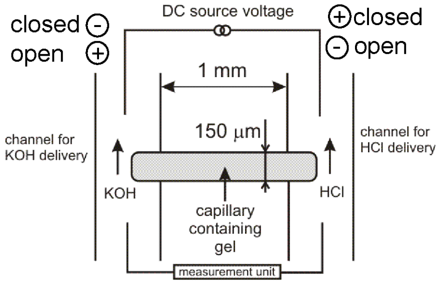

Fig. 1 Scheme of the electrolyte diode system.

2. Mathematical model and numerical analysis

The mathematical model of the electrolyte diode consists of four mass balances of ionic components

$$\frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial x}\left(-D_i \frac{\partial c_i}{\partial x} - \frac{z_i c_i D_i F}{RT}\frac{\partial \Phi}{\partial x}\right) + \nu_i r\,, \tag{1}$$

where, the index i can represent potassium, chloride, hydrogen, and hydroxyl ions. Poisson equation of electrostatics is used for the evaluation of the electric potential distribution

$$\varepsilon \frac{\partial^2 \Phi}{\partial x^2} = -F \sum_i z_i c_i\,. \tag{2}$$

The symbols c_i, D_i, z_i, ν_i, F, R, T, Φ, ε denote ionic concentration, ionic diffusivity, ionic charge number, stoichiometric coefficient of the ion i in the chemical reaction, Faraday's constant, molar gas constant, temperature, electric potential and permittivity of the environment, respectively. The reaction rate of water formation r is defined as

$$r = -k\left(K_w - c_{H^+} c_{OH^-}\right), \tag{3}$$

where symbols k and K_w represent the kinetic and the equilibrium constants of water formation, respectively. Eqs. (1) and (2) together with Dirichlet boundary conditions form the studied mathematical model. Cf. also the Model A section in Lindner et al. (2002) for detail explanation and for the discussion of the used parameter values.

Large moving gradients of electric potential and ionic concentrations bring problems in numerical analysis of the electrolyte diode. Hence both the stationary and the dynamical solvers use a mesh adaptation technique (Přibyl et. al., 2005). The sudden changes of the difference of electric potential, when the non-stationary behavior is studied, are modeled as a fast linear decrease or increase of electric potential on one boundary. The duration of the linear change was set to 0.1 second.

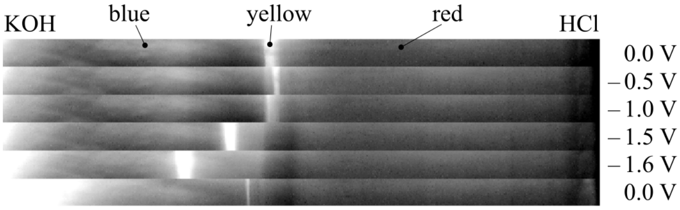

Fig. 2 Dependence of the position of the zone with low electric conductivity on the imposed difference of electric potential. The zone is depicted by a light (yellow) stripe.

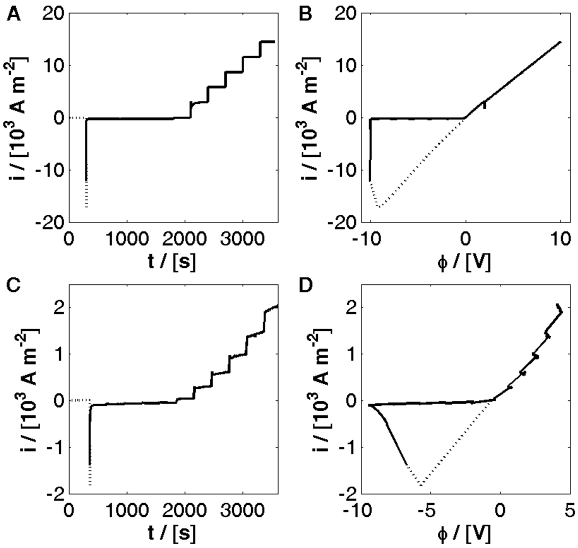

Fig. 3 Opening the electrolyte diode. Time courses of electric current density obtained from numerical analysis (A) and experiments (C). Corresponding current-voltage characteristics (B,D).

3. Experimental arrangement

The electrolyte diode is constructed from two polystyrene plates. The plates are manufactured by a micro-milling machine. Two channels forming the flow-through reservoirs of the acid and the base are drilled in the upper plate. The connecting microcapillary is milled into the bottom plate. A dried and shrunk piece of the polyvinylalcohol gel (PVA, Fluka) is inserted into the microcapillary. Then the plates are pressed together and connected by thermosetting in a furnace (15 minutes, 90 °C). When the polystyrene device is cooled, a water electrolyte is supplied into the gel that swells and tightly fills the microcapillary. Finally, the measuring and the source electrodes are inserted into the microchip. To obtain the current-voltage characteristics of the electrolyte diode, the imposed potential difference is increased or decreased in specified time intervals and the current response is recorded.

4. Results and discussion

4.1. Steady state behavior

If the electrolyte diode is in the closed mode, the narrow zone of low electrolyte conductivity is characterized by a large gradient of pH. This gradient can be detected by a pH sensitive dye, for example, thymol blue (see Fig. 2). Differences of electric potential were applied on the capillary boundaries and the positions of the large pH gradients were observed. If the applied voltage is negative, the gradient shifts closer to the alkaline reservoir due to difference between the diffusivities of hydrogen and hydroxyl ions (in water $D_H = 9.31\times10^{-9}$ m^2s^{-1}, $D_{OH} = 5.28\times10^{-9}$ m^2s^{-1}). However, the used color indicator brings ionic impurity into the electrolyte diode system. Hence the experimentally observed results are affected by the electromigration transport of thymol blue ions. Numerical results of the stationary analysis of the electrolyte diode are described in Lindner et al. (2002).

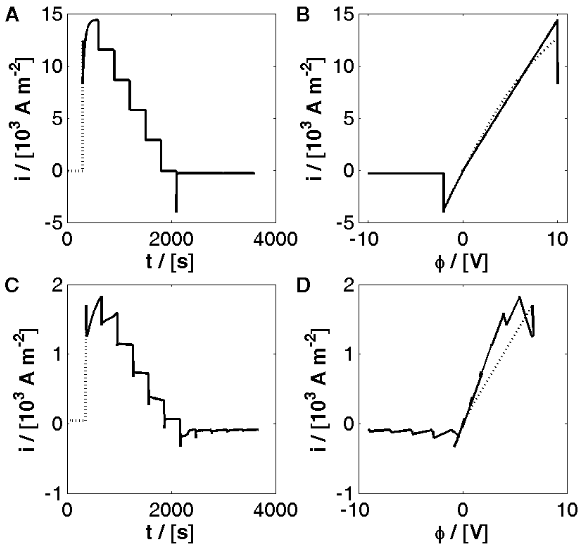

Fig. 4 Closing the electrolyte diode. Time courses of electric current density obtained from numerical analysis (A) and experiments (C). Corresponding current-voltage characteristics (B,D).

4.2. Numerical and experimental analysis of electrolyte diode transient behavior

The dynamical analysis starts in the steady state when no difference of electric potential is applied. After every 300 seconds, the applied difference is switched to another value. The transient response of the system is recorded.

First, the transition of the electrolyte diode to the closed mode and its consecutive opening was studied. The following sequence of electric potential differences was used: 0, -10, -8, -6, -4, -2, 0, 2, 4, 6, 8, 10 Volts. The observed transient behavior of the electrolyte diode expressed as the computed/measured electric current density is plotted in Fig. 3. Figs. 3A, B were obtained by numerical analysis of the model equations and the results in Figs. 3C, D were recorded during the experiment. The time courses of the observed electric current are shown in Figs. 3 A, C. The transition of the electrolyte diode into the closed mode at time 300 s is accompanied by a short-time overshoot of electric current density. Then the dependencies are characterized by low values of electric current density when a negative voltage is applied (closed mode). In the open mode, the observed electric current density is linearly proportional to the applied potential difference (see Figs. 3 B, D). The current-voltage characteristics obtained by numerical and experimental analyses are in good qualitative agreement. However the absolute values of electric current density differ because of a decrease of ionic diffusivities in the PVA gel with respect to the values for dilute water solutions (considered in the simulations). The decrease leads to the reduction of both the diffusion and the electromigration fluxes of ions and thus to lower values of electric current density.

The transition of the electrolyte diode to the open mode and its consecutive closing was studied in the next step (Fig. 4). The following sequence of the difference of electric potential was used: 0, 10, 8, 6, 4, 2, 0, -2, -4, -6, -8, -10 Volts. Two significant overshoots of electric current density are observed (Figs. 4A, C). The overshoots occur when: (i) the diode is switched to the open mode at time 300 s and (ii) the imposed electric potential difference varies from 0 V to -2 V at time 2100 s. The corresponding current-voltage characteristics are plotted in Figs. 4B, D.

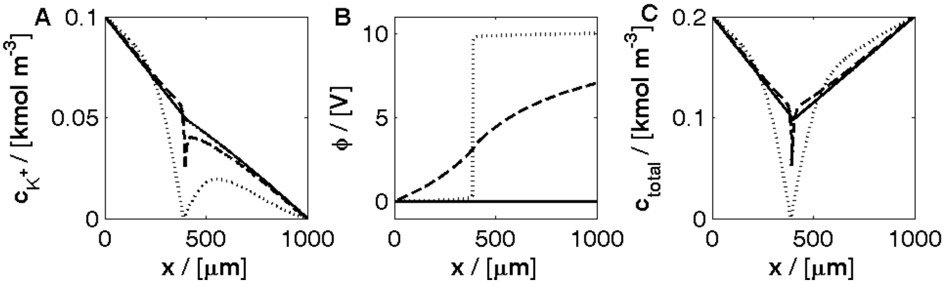

Fig. 5 Electric current density overshoot – switch to the closed mode. Spatial profiles of potassium concentration (A), electric potential (B) and the total ionic concentration (C). The profiles are plotted in 300 s (solid line), 300.07 s (dashed line) and 302 s (dotted line) after the start of numerical simulation.

The two experimentally obtained current-voltage dependencies somewhat differ (compare Figs. 3D, 4D). This is caused by the concentration polarization of the source electrodes that leads to the decrease of the voltage actually imposed on the microcapillary.

4.3. Analysis of transient overshoots

The current density overshoot in Figs. 3A, C at time of 300 s can be explained by the analysis of spatio-temporal distributions of model variables obtained from the numerical analysis. Distributions of potassium ions, electric potential and the total ionic concentration (the sum of concentrations of all ions) before the decrease of voltage difference from 0 Volts to -10 Volts are depicted by solid lines in Figs. 5A-C, respectively. When the potential difference is increased, the electric current density grows according to Ohm’s law (dashed line). Consequently, chloride and potassium ions start to migrate out of the system and thus hydrogen and hydroxyl ions become dominant. Their neutralization in the microcapillary leads to the formation of the zone with extremely low electric conductivity where almost no ions are located. Hence the electric potential drop is concentrated within the thin zone (dotted line). The observed value of electric current density returns close to zero and the electrolyte diode approaches the closed mode.

The nature of the current density overshoot in Figs. 4A, C at the time 300 s can be explained as follows: The increase of voltage difference from 0 Volts to 10 Volts is accompanied by a growing electromigration transport of the ionic components, which result in an increase of the electric current density (dashed line in Fig. 6). Potassium and chloride ions are transported into the microcapillary whereas hydrogen and hydroxyl ions remain close to their reservoirs. The microcapillary then behaves as a globally electroneutral system. Hence, for example, the concentration of potassium cations migrating from the KOH reservoir cannot exceed the concentration of chloride anions everywhere in the microcapillary except in the regions close to the reservoirs. This reflects the fact that hydrogen and hydroxyl ions in the centre of the microcapillary vanish and their concentration is close to 10^{-7} kmol m^{-3} that is characteristic for water. In the early stage after the voltage shift, it results in a decrease of the total ionic concentration, an increase of the electric resistance and a decrease of the electric current density (dotted line in Fig. 6). As chloride and potassium ions further migrate into the microcapillary, the total ionic concentration again increases (dash-dotted line in Fig. 6), which is accompanied by the observed increase of the electric current density.

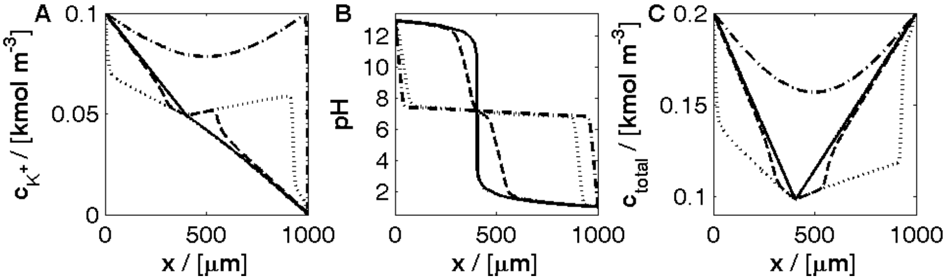

Fig. 6 Electric current density overshoot – switch to the open mode. Spatial profiles of potassium concentration (A), pH value (B) and the total ionic concentration (C). The profiles are plotted in 300 s (solid line), 300.07 s (dashed line), 300.3 s (dotted line) and 350 s (dash-dotted line) after the start of numerical simulation.

5. Conclusions

Numerical analysis and experiments carried out on the electrolyte diode system reveal a complex transient behavior. Detailed numerical analysis of the reaction-transport processes in the electrolyte diode explains the short-time overshoots in the current-voltage characteristics when the system is switched into the open and/or the closed mode. The obtained experimental results are in a good qualitative agreement with the results of modeling, which supports correctness of the used mathematical description. The discrepancies between the modeling results and experiments are primarily caused by the use of approximate values of ionic diffusivities in the model. The spatially one-dimensional approximation of the real three-dimensional system that can contain, e.g., spatial heterogeneities in the porous structure is the other reason for the differences.

6. Acknowledgement

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References

L. Hegedüs, Z. Noszticzius, A. Papp, A.P. Schubert, M. Wittmann, 1995, ACH - Models in Chemistry, 132, 1-2, 207-224.

L. Hegedüs, N. Kirschner, M. Wittmann, Z. Noszticzius, 1996, Progress in Colloid and Polymer Science, 102, 101-109.

L. Hegedüs, N. Kirschner, M. Wittmann, Z. Noszticzius, 1998, Journal of Physical Chemistry A, 102, 6491-6497.

J. H. Merkin, P.L. Simon, Z. Noszticzius, 2000, Journal of Mathematical Chemistry, 28, 1-3, 43-58.

J. Lindner, D. Šnita, M. Marek, 2002, Physical Chemistry Chemical Physics, 4, 1348-1354.

M.Přibyl, D. Šnita, M. Marek, 2005, Chemical Engineering Journal, 105, 99-109.

D. Šnita, M. Pačes, J. Lindner, J. Kosek and M. Marek, 2001, Faraday Discussions, 120, 53-66.