Acid-base diodes in a hydrogel medium.
Nonlinear response for mono- and divalent contaminating ions: theory and experiments

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SUMMARY: Small hydrogel cylinders connecting aqueous solutions of a strong acid and a strong base show a current-voltage characteristic similar to that of a semiconductor diode. This characteristic is affected by adding a salt either to the acid or to the base and the response is highly nonlinear close to certain critical salt concentrations. Theoretical characteristics derived from the Nernst-Planck equations agree qualitatively with the experimental observations for moderate salt concentrations. Applying higher salt concentrations, however, deviations can be observed which are similar in character for both mono- and divalent contaminating ions. The results suggest that the deviation from the theoretical behaviour is not due to ion specific properties, but rather it is caused by the hydrogel medium itself.

Introduction

An electrolyte diode [1-2] can be constructed by connecting reservoirs of a strong acid and a strong base with a hydrogel cylinder. In the present experiments we applied poly(vinyl-alcohol)- glutardialdehyde hydrogels. A schematic cross-sectional view of the experimental apparatus is shown in Fig. 1.

In the forward direction (polarity: the alkaline reservoir is positive) the electric current is carried mainly by the cations of the base and the anions of the acid, and these ions form a well-conducting salt solution in the gel. In the reverse direction (polarity: the alkaline reservoir is negative) the hydrogen and hydroxyl ions, which recombine and form a thin layer of pure water with high impedance, carry the current. The current density *i* in the reverse direction can be given by the following formula [1] according to the Nernst-Planck equations:

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$$i=\frac{F}{L}\cdot\left(D_H+D_{OH}\right)\cdot\left[2c_0+\sqrt{K_w}\Delta\varphi\right] \tag{1}$$

where F: the Faraday number, L: length of the gel cylinder, D_H and D_{OH} : individual diffusion coefficients of the hydrogen and hydroxyl ions, respectively, c_0: concentration of the acid and

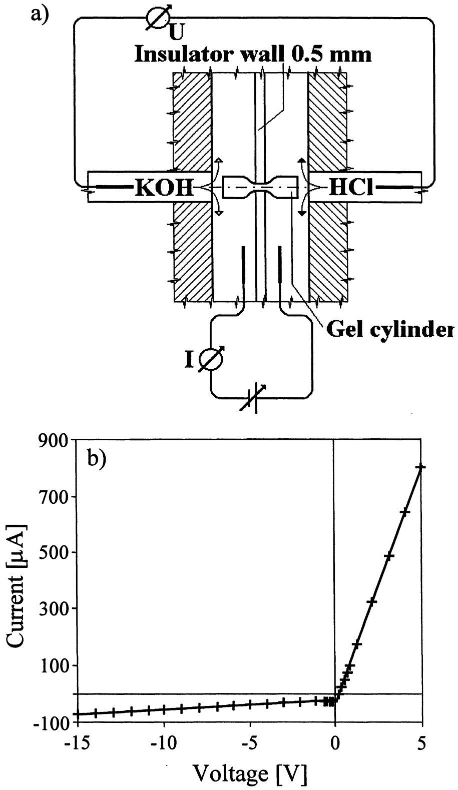


Fig. 1. An electrolyte diode experiment
a) The gel cylinder and its immediate neighbourhood. The reservoirs and the electrode pairs for current and voltage measurements are shown only schematically here. A continuous flow of KOH and HCl solutions maintains a steady concentration gradient in the gel cylinder. For further details of the apparatus and the preparation of the hydrogel cylinder see [1)]
b) Current-voltage characteristic of the diode.

the alkaline reservoirs (here c_0 = [HCl] = [KOH] = 0.1 M), K_w: ionic product of the water, $\Delta\varphi$: dimensionless voltage. Most gels contain fixed anions. In this case (1) is modified:

$$i=\frac{F}{L}\cdot D_H\cdot\left[2c_0\left(\frac{D_{OH}}{D_H}+1\right)+c_{FA}\Delta\varphi\right] \tag{2}$$

where c_{FA} is the concentration of the fixed anions in the gel.

When a contaminating salt is added to the alkaline or to the acidic reservoir of a reverse biased diode, the current response is highly nonlinear and even bistability can be observed in certain cases. Namely, as the salt concentration is increased, first the reverse current is not affected in a wide concentration region but close to a critical concentration the current starts to grow rapidly. This nonlinear salt effect is studied here first for monovalent then for divalent ions.

Salt contamination in the alkaline reservoir

For monovalent ions, when the salt (here KCl) is added to the alkaline reservoir, (2) has the following form 3):

$$i = \frac{F}{L} \cdot D_H \cdot \left(1 + \mu_1 \frac{D_{Cl}}{D_H}\right)\left[2c_0\left(\frac{D_{OH}}{D_H} + \frac{1}{1-\mu_1}\right) + \frac{c_{FA}}{1-\mu_1}\Delta\varphi\right] \tag{3}$$

where

$$\mu_1 = \frac{D_H}{D_{OH}} \cdot \frac{c_s}{c_0} ,$$

c_s: KCl concentration in the alkaline reservoir, D_{Cl}: diffusion coefficient of the chloride ions.

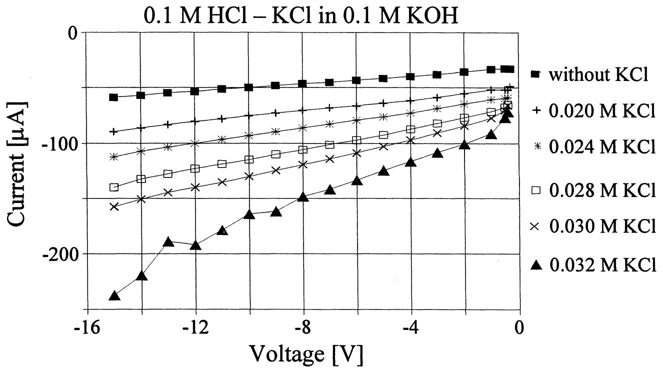


Fig. 2. Polarisation curves with different KCl concentrations added to the KOH reservoir (c_0 = 0.1 M)

When μ_1 is small, then the reverse current calculated by (3) is close to the one given by (2). On the other hand, when μ_1 is close to 1 then both the slope and the intercept of the i vs. $\Delta\varphi_{OH}$ characteristics should grow rapidly. This theoretical prediction was in good qualitative agreement with the experiments for moderate μ_1 values (see Fig. 2. for comparison). Both the slope and the intercept of the i vs. $\Delta\varphi$ (current-voltage) characteristics grew with μ_1 as expected.

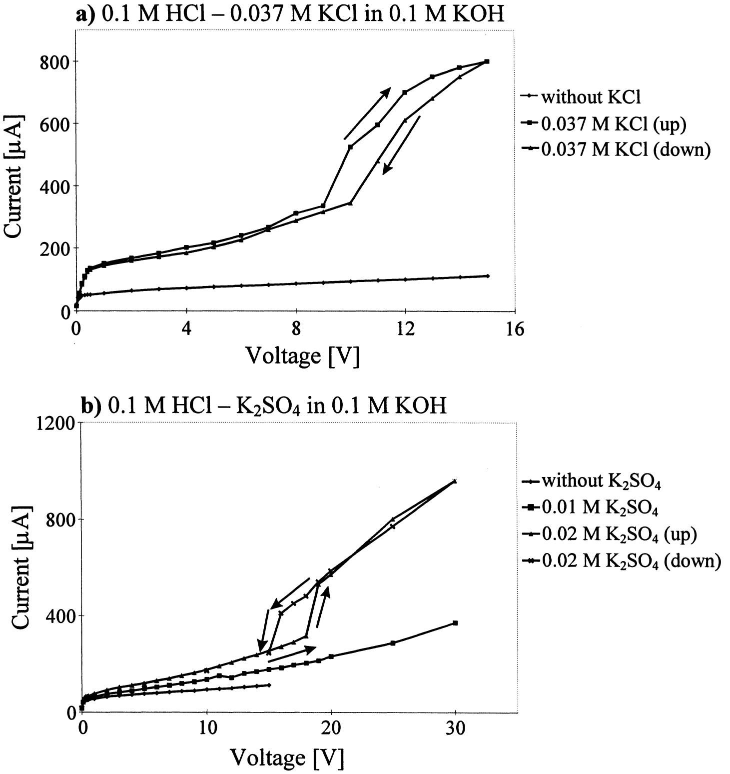


Fig. 3. Breakpoint in the current-voltage characteristic of an acid-base diode (c_0 = 0.1 M) with high salt contamination in the alkaline reservoir
a) monovalent contaminating anion (chloride), c_s = 0.037 M
b) divalent contaminant (sulphate), c_s = 0.01 - 0.02 M

When μ_1 was close to 1, however, the measured current-voltage characteristic displayed the expected behaviour only for lower voltages. At higher voltages a breakpoint appeared beyond which the slope was much higher (Fig. 3a). To prove that this phenomenon is not due the contaminating ion (here: chloride ions) we repeated the experiment with divalent sulphate ions. For this case the following formula can be derived [4]:

$$i = \frac{F}{L} \cdot D_H \cdot \left(1 + 3\mu_1 \frac{D_{SO_4}}{D_H}\right) \left[2c_0 \left(\frac{D_{OH}}{D_H} + \frac{1.5}{2 - 3\mu_1} \right) + \frac{2c_{FA}}{2 - 3\mu_1} \Delta\varphi \right] \tag{4}$$

As it can be seen, the critical μ_1 is not 1 like in the case of monovalent ions but 2/3. Thus divalent ions are 3/2 times more effective than the monovalent ones. Our experimental results were in agreement with these theoretical considerations but close to the critical $\mu_1 = 2/3$ value, a similar breakpoint was found in the current-voltage characteristics like for monovalent ions (Fig. 3b).

Salt contamination in the acidic reservoir

When the contaminating salt is added to the acidic reservoir, the analogous expression to (3) is (5) (the contaminating monovalent ion is K^+ here):

$$i = \frac{F}{L}\cdot D_H \cdot \left(1+\mu_2 \frac{D_K}{D_{OH}}\right)\left[2c_0\left(1+\frac{D_{OH}/D_H}{1-\mu_2}\right)+\frac{D_{OH}}{D_{OH}+D_H\mu_2}c_{FA}\Delta\varphi\right] \qquad (5)$$

where $\mu_2 = \frac{D_{OH}}{D_H}\cdot\frac{c_s}{c_0}$.

Experimental results are displayed in Fig. 4.

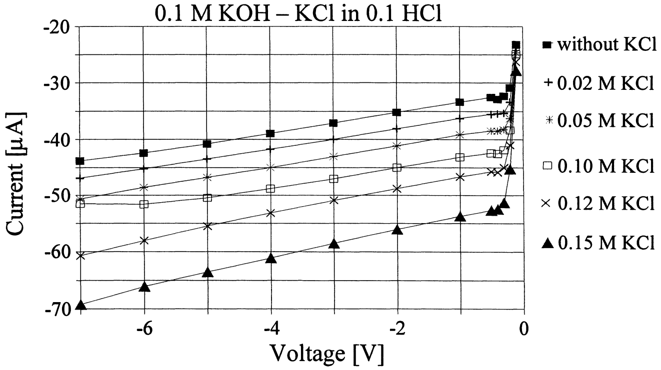
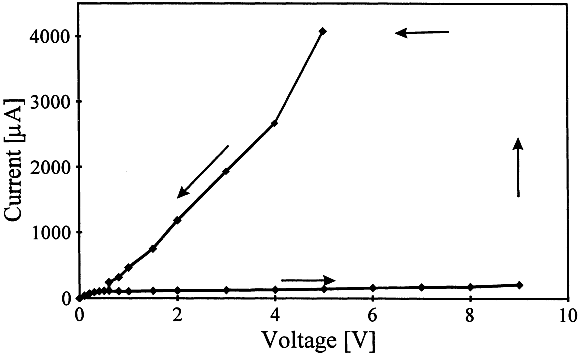


Fig. 4. Polarisation curves with different KCl concentrations added to the HCl reservoir ($c_0 = 0.1$ M)

For moderate μ_2 values experiments and theory were in good qualitative agreement [5] again: the intercept of the current-voltage characteristic grew with the increasing μ_2 while the slope remained constant or decreased slightly. On the other hand, when μ_2 was close to 1 an unexpected bistability appeared (see Fig. 5a), and the same behaviour was observed with divalent Ba^{2+} ions as well as shown in Fig. 5b. Theoretical effect of the latter contaminating cations on current-voltage characteristics [4] is given by (6).

$$i = \frac{F}{L}\cdot D_H \cdot \left(1+3\mu_2 \frac{D_{Ba}}{D_{OH}}\right)\left[2c_0\left(1+\frac{1.5D_{OH}/D_H}{2-3\mu_2}\right)+\frac{2D_{OH}}{2D_{OH}+3D_H\mu_2}c_{FA}\Delta\varphi\right] \qquad (6)$$

a) 0.1 M KOH – 0.2 M KCl in 0.1 M HCl



b) 0.1 M KOH – 0.1 M $BaCl_2$ in 0.1 M HCl

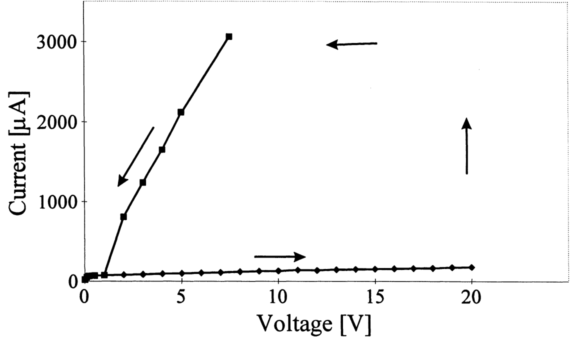


Fig. 5. Bistability of the electrolyte diode (c_0 = 0.1 M) with high salt contamination in the acidic reservoir
a) monovalent contaminating cation (potassium), c_s = 0.02 M
b) divalent contaminant (barium), c_s = 0.01 M

Conclusion

Experimental and theoretical current-voltage characteristics of acid-base diodes in a hydrogel medium show a good agreement when moderate contaminating salt concentrations are established in the alkaline or in the acidic reservoir. At close to critical salt concentrations, however, new phenomena - like break points in the characteristics associated with some hysteresis like memory effects or even strong bistability - appear. These deviations from the theory are not to be explained with the individual ionic properties as similar deviations were found for mono- and divalent contaminating ions as well. Most probably, it is the hydrogel itself, which is responsible for these complex phenomena, and future research should focus on this problem.

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References and notes

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4. Further theoretical considerations regarding multivalent ions including the derivation of this formula will be published elsewhere: N. Kirschner, P.L. Simon, M. Wittmann, Z. Noszticzius, J. Merkin: work in progress.
5. A more quantitative comparison of the theoretical and experimental curves would require the exact values of the individual ionic diffusion components in the gel medium, which are not available presently.