Nonlinear phenomena of electrolyte diodes and transistors

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The polarization curve of an acid-base interface in a hydrogel medium has a diode characteristic. Two of such electrolyte diodes can be combined to give an electrolyte transistor. When salt is added to the alkaline or to the acidic part of a reverse biased electrolyte diode, the current response is highly nonlinear. If the salt is added to the acidic side, even bistability can be observed. This bistability can generate complex oscillations in a base-acid-base electrolyte transistor. These nonlinear effects are studied experimentally. Small salt concentrations have practically no effect but the diode current increases drastically in the neighbourhood of a critical salt concentration.

I. BACKGROUND

A. The electrolyte diode

The electrolyte diode is an open chemical system where simultaneous concentration and electric potential gradients are maintained in a polymer gel medium. In the experimental apparatus a small hydrogel cylinder (see Fig. 1a) connects an alkaline and an acidic chamber fed continuously by fresh KOH and HCl solutions. The current-voltage characteristic of such a system (Fig. 1b) resembles to that of a semiconductor diode. In the case studied here a polyvinyl alcohol glutardialdehyde gel[1,2] connects potassium hydroxide and hydrochloric acid solutions of the same c_0 concentration.

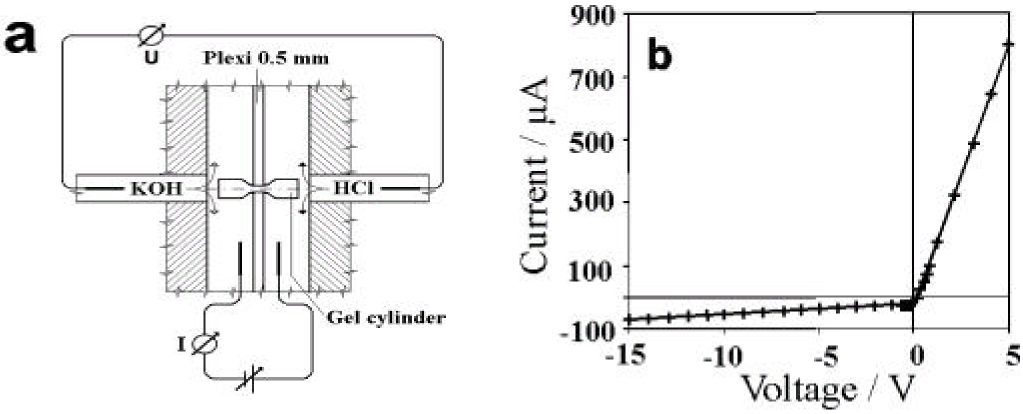

Figure 1

At positive (forward) voltages potassium ions from the alkaline solution and chloride ions from the acidic one migrate into the gel and form a 0.1 M KCl solution there. In this case of the forward biased diode the electric current density is proportional to the applied voltage[1].

The situation in the reverse direction is qualitatively different. Now Cl^- and K^+ ions migrate out of the middle region of the gel. In steady state a very thin zone of pure water is formed between the acidic and the alkaline regions of the gel. In this neutral zone $c_H = c_{OH} \approx \sqrt{K_W} = 10^{-7}$M, where K_w is the ionic product of water. For large reverse voltages most of the voltage drop occurs in this high impedance zone of pure water.

Now the H^+ and OH^- ions carry most of the electric current and the contribution of K^+ and Cl^- ions is negligible. The gel can be divided into three parts: an alkaline, a neutral and an acidic one. In the alkaline region the current is carried mainly by OH^- ions, in the thin neutral zone both OH^- and H^+ ions contribute to the current, and in the acidic region H^+ ions carry most of the current. According to this simplified picture, recombination of H^+ and OH^- ions takes place at the two interfaces of the three different regions mentioned above. When experimental current-voltage characteristics measured on PVA based hydrogel cylinders were compared to the theoretical ones, a good agreement was found in the forward direction. In the reverse direction, however, the measured slope of the current-voltage curves were orders of magnitude higher than expected. It was found that fixed anions in the gel are responsible for the observed high reverse currents.

B. The electrolyte transistor

An electrolyte transistor can be constructed from two electrolyte diodes in a similar way like its semiconductor counterpart[3]. To understand the transistor action first we should consider what happens with the current of a reverse biased electrolyte diode if some salt is added to its alkaline or acidic reservoir. As it was shown in the previous paragraph, in the case of pure acidic and alkaline solutions in the middle of the diode a thin layer of low electrolyte concentration is formed. Due to the high impedance of this layer the electric current is relatively small. If the acid or the base is not pure but contains also some dissolved salt (e.g. KCl) this can increase the current in the reverse biased diode considerably. For example if chloride ions are mixed into the KOH solution these contaminating ions can migrate into the depletion zone increasing its conductivity because unlike the H^+ and OH^- ions they are not able to recombine in the depletion region. This ”salt effect” due to the contaminating ions is applied as the working principle of the electrolyte transistor. Let us regard an acid-base-acid (SLS) transistor first. (S stands for acidic and L for alkaline solutions to avoid possible ambiguities in the notation.) Physically this is also a hydrogel cylinder (diameter 0.8 mm) connecting three electrolyte solutions (0.1 M HCl-0.1 M KOH-0.1 M HCl). The three solutions are separated by two thin (0.5 mm) plexi-glass walls with holes for the gel (Fig. 2a). The gel plug prevents any convective transport between the compartments but allows diffusion and electric migration of ions. To maintain constant concentrations in the three compartments a continuous flow of fresh electrolyte solutions is applied in each of them. The middle compartment is narrow: the distance between the two plexi-glass walls is only 0.5 mm. This is important to achieve the transistor action. In the active mode the first diode (the emitter-base diode) is biased in the forward direction while the second one (the base-collector) is biased reversely. In this case chloride ions from the first acidic reservoir migrate into the narrow alkaline zone in the middle. If this zone is narrow then most of these contaminating chloride ions do not diffuse out of the gel there but continue to migrate across the reverse biased base-collector junction. This is the transistor action, when carriers from the forward biased emitter-base diode generate a current in the reverse biased base-collector diode[4]. The transistor action was demonstrated first with an SLS transistor in the ”common base” configuration. One of the diodes was chosen as “base-collector” diode. A constant reverse bias (-10 V) was applied here. The voltage on the other “base-emitter” diode (U_{BE}) is the independent variable of the experiment and the three different currents (I_E, I_C, I_B) were measured as a function of this variable. The measured transistor characteristic is shown in Fig. 2b. While the emitter-collector is reverse biased (cutoff mode) I_C is independent of U_{BE}, but - as a result of the transistor action - I_C starts to grow monotonically with U_{BE} when the emitter-collector junction is forward biased (active mode).
The complement of the SLS transistor is the LSL transistor. In the active mode, however, above a certain U_{EB} voltage the LSL transistor is unstable and exhibits complex oscillations. This unexpected behavior initiated mainly our present investigations and it will be studied experimentally in the following chapter.

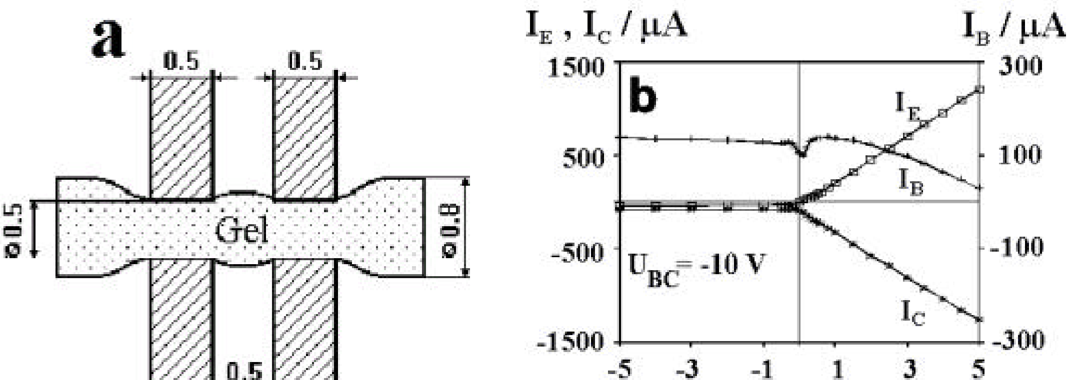

Figure 2

II. EXPERIMENTS

A. Complex oscillations in the LSL transistors

As it was mentioned the LSL transistor is unstable in its active mode and displays regular and irregular complex oscillations depending on the emitter-base voltage. This behavior is illustrated in Fig. 3. An important aim of the present paper is to investigate the source of this instability leading to oscillations in the LSL transistor. As we know the SLS transistor, on the other hand, is a stable amplifying device. Thus it would be also important to find an explanation for this qualitatively different behavior of the SLS and LSL transistors. In the active mode the base layer of both transistors is contaminated by some salt. This is due to the emitter current driving Cl^- or K^+ ions to the base layer of an SLS or LSL transistor, respectively. This salt contamination of the base will increase the current of the reverse biased base-collector diode.

The only difference between the SLS and LSL transistors is that in the first case it is the alkaline side of the base-collector diode which is contaminated with KCl while in the second case this is the acidic side. Thus the qualitative difference between the SLS and LSL transistors should be associated with a qualitatively different response of an electrolyte diode when some salt is added to its alkaline or acidic side. Following this logic in the next paragraphs we study the effect of KCl added to the alkaline or acidic feedstream of a reverse biased electrolyte diode.

B. Response of an electrolyte diode to salt contamination

1. Salt added to the alkaline feedstream

For the experiments we used an electrolyte diode similar to the one depicted in Fig. 1. A constant reverse bias (-2 V) was used and the reverse current was measured as a function of the salt concentration in the alkaline feedstream. KOH and HCl concentrations were kept constant (0.1 M) and the salt concentration was increased in small steps, mixing more and more salt to the alkaline solution[5]. The diode current as a function of the salt concentration in the alkaline feedstream is shown in Fig. 4. As we can see the response is continuous but rather nonlinear: the curve has an inflection point and a maximal slope around 0.04 M KCl concentration.

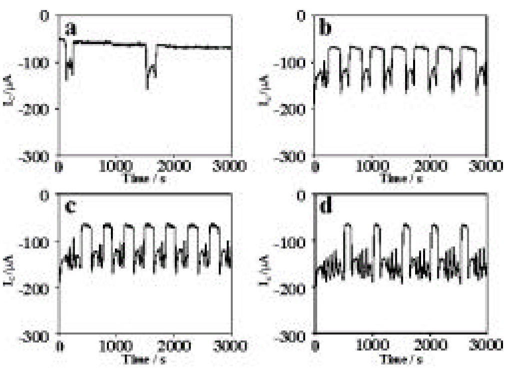

Figure 3

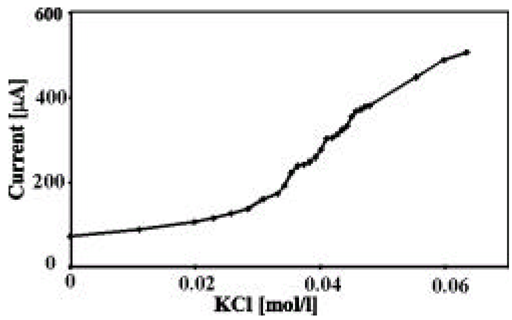

Figure 4

2. Salt added to the acidic feedstream. Bistability

When the salt was added to the acidic feedstream the experiment gave a qualitatively different result (see Fig. 5). The response was highly nonlinear here and there was even a "jump" in the current at 0.25 M KCl concentration. Decreasing the salt concentration reveals a hystheresis loop, which is a characteristic feature of bistable behavior. The current falls back to the original branch only at 0.18 M KCl concentration.

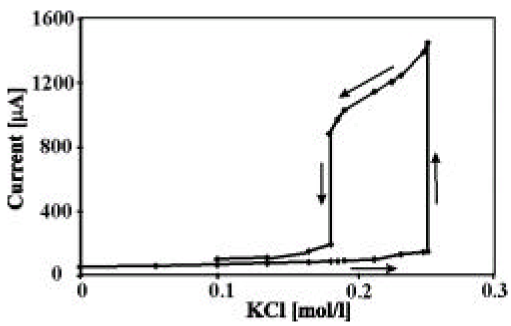

Figure 5

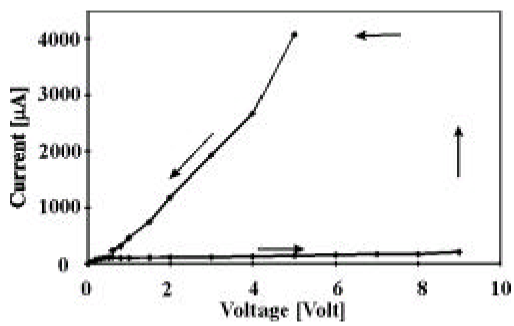

Figure 6

To demonstrate bistability at a certain fixed concentration (0.232 M somewhere in the middle in the bistable region of Fig. 5) with an independent method a voltage-current hystheresis loop is presented in Fig. 6. In this experiment the lower branch of the current-voltage characteristic was measured first by increasing the potential step by step. When the current jumped up at 9 V the voltage was decreased immediately to 5 V. This was

necessary to avoid an otherwise too high dissipation in the depletion zone of the diode. Then the higher branch of the characteristic was measured by decreasing the potential gradually.
Summarizing our experimental observations we can conclude that the electrolyte diode gives a nonlinear response to the salt added to both the alkaline and the acidic feedstreams but this response is qualitatively different in the two cases: bistability occurs only if the salt is added to the acid.

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[4] Naturally the electrolyte transistor is not completely analogous to the classical transistor when all details of the transistor action are regarded. An important difference is that while holes are able to diffuse through a narrow n-type semiconductor region, H^+ ions cannot avoid recombination with OH^- ions when moving through an alkaline zone. Thus the H^+ ions can permeate through the base region only by establishing a narrow acidic channel inside it. The counterions in this case are the Cl^- ions migrating in the opposite direction. In this respect the electrolyte transistor resembles more to a field-effect transistor than to its classical counterpart.

[5] Two peristaltic pumps were applied to prepare the mixed feedstream. One of them was pumping a pure 0.1 M KOH (or HCl) solution, while the other was pumping a mixture (concentrations: 0.1 M base or acid, and 0.1 M KCl in the mixture) with a variable rate.

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FIGURE CAPTIONS

Fig. 1. An electrolyte diode experiment
a) The gel cylinder and its immediate neighbourhood. The electrode pairs for current and voltage measurements are shown only schematically.
b) Current-voltage characteristic of the diode.
Fig. 2. Experiments with an acid-base-acid (SLS) type electrolyte transistor
a) The gel cylinder and its surrounding.
b) Current-voltage characteristics of an SLS transistor measured at fix base-collector voltage (U_{BC} = -10 V) in common base configuration. Emitter (I_E), collector (I_C) and base (I_B) currents are shown as a function of the base-emitter (U_{BE}) voltage. Observe that in the active mode of the transistor (when U_{BE} is positive) I_C is not constant but varies with U_{BE}.
Fig. 3. Excitability and complex oscillations of the collector current I_C in the active mode of an LSL transistor at various base-emitter voltages. Common base configuration, U_{CB} = -10 V.
a) U_{EB} = 1.2 and 1.3 V. There are no oscillations in the transistor but it is excitable. This means that the steady state is stable but perturbations above a certain threshold can initiate a nonmonotonous response of the system. The first peak appeared when U_{EB} was increased stepwise from 1.1 to 1.2 V. The second one was initiated by the next increase from 1.2 to 1.3 V.
Complex oscillations at **b)** U_{EB} = 1.4 V, **c)** U_{EB} = 1.5 V, **d)** U_{EB} = 1.7 V. The oscillations exhibit a regular pattern except for a transient period at the beginning. The period and the average current grows with time.
Fig. 4. Nonlinear salt effect in a reverse biased (U = -2 V) electrolyte diode. Salt added to the alkaline feedstream. It is the absolute value of the reverse current , $|I|$, which is shown in the Figure.
Fig. 5. Nonlinear salt effect and bistability in a reverse biased (U = -2 V) electrolyte diode. $|I|$ vs. c diagram. Salt added to the acidic feedstream.
Fig. 6. Bistability in the voltage-current characteristic of a contaminated electrolyte diode.
$|I|$ vs. $|\Delta\varphi|$ diagram. The acidic feedstream contains 0.2 M KCl besides the usual 0.1 M HCl.