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Electrolyte Transistors: Ionic Reaction−Diffusion Systems with Amplifying Properties

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The problem of constructing chemoelectric amplifying devices based on acid−base reactions is discussed. It is shown that the construction of a direct analogue of the semiconductor transistor (that is, when the p- and n-doped semiconductors are replaced by ion exchange membranes in the H^+ and OH^- forms, respectively) is technically not feasible. The new amplifying device reported here is based exclusively on mobile ions migrating in a hydrogel arrangement that contains no fixed charges. The polarization curve of an acid−base interface in this medium has a diode characteristic. When two of such "electrolyte diodes" are connected appropriately, a transistor action can be observed: the electric current flowing in one (reverse biased) diode is affected not only by the voltage applied there but also by the current flowing through the other (forward biased) diode. The common emitter current gain of an acid−base−acid transistor studied here was between 4 and 5. The active mode characteristics of this device can be explained by the appearance of an acidic tunnel across the alkaline middle section. Although the acid−base−acid transistor is a stable amplifying device, the base−acid−base transistor is unstable in its active mode and displays complex oscillations. The underlying bistable behavior was also demonstrated with this transistor when its acidic feedstream was contaminated with KCl.

Introduction

Background. An important trend in the present day research of nonlinear chemical systems[1] is increasing their complexity.[2] Complex systems have interacting components whose collective behavior cannot be simply inferred from the behavior of their components.[3] The purpose of this type of research is to observe new nonlinear phenomena and/or to mimic the behavior of the more complex biological systems. This trend can be followed, for example, in the evolution of the various reactors applied in the experiments. The first typical nonlinear phenomena in chemistry—namely, oscillations[4−7] and waves[6−9]—were discovered and studied originally in simple closed batch reactors. Later, to sustain far-from-equilibrium conditions, open reactors such as CSTRs (continuously fed stirred tank reactors) and CFURs (continuously fed unstirred reactors) were introduced to study the temporal behavior in homogeneous reacting systems[10,11] and spatial−temporal patterns in reaction−diffusion experiments,[12−18] respectively. Especially CFURs can be rather structured that is, complex devices. They usually contain a gel medium to prevent convection in the reactor that would destroy the reaction−diffusion patterns. Besides gels, membranes also play an important role in living systems as structural elements. Various membranes are also applied in open reactors[19−24] mainly to fix the catalyst, but selective feeding of certain chemical components via membranes is also known.[25,26] With this new gel and membrane technology complex devices such as a chemical diode[27] and logic gates for chemical waves[28] were constructed recently. These are important results because they demonstrate that not only signal transmission but also signal processing—as in biological systems or in electronic circuits—is also possible with reaction−diffusion systems and complex reactors.

Aims of this Work. Inspired by the above-mentioned chemical diode and logic gates experiments, we decided to investigate the problem of signal amplification by complex reaction−diffusion systems. At the same time we wanted to move closer to the (i) physical and (ii) chemical conditions characterizing real biological systems.

(i) Physical Conditions. It is important to observe that purely chemical waves are much slower than the biological ones such as the neural signal transmission or the speed of the activity fronts in the heart muscle. The higher speed of the biological waves is due to an interplay of chemical and electric processes. As a consequence, besides the local concentrations of certain chemical intermediates, transmembrane electric potential is also an important variable in excitable biological systems.[29] It is worth mentioning that in the presence of electric potential gradients, various complex phenomena can be observed in artificial membranes as well.[30,31] Thus, our aim here is to create a device that is not entirely chemical in nature (like the above-mentioned chemical diode or logic gates); electric potential is also an important variable/parameter of the system.

(ii) Chemistry. Present nonlinear experiments are dominated by halogen and sulfur chemistry because self-accelerating reactions necessary for chemical instabilities are easier to find in this field. Although these experiments are important to understand certain general principles, their chemistries are alien to real biological systems. The acid−base reactions in pH oscillators[32,33] are exceptional, since H^+ and OH^- ions play an important role in living systems too. In pH oscillators, however, the acid−base reactions are coupled again with halogen- or sulfur-based redox reactions. To avoid such "nonbiological" reactions here, we try to base our new amplifying device exclusively on the $H^+ + OH^- \leftrightarrow H_2O$ reaction. Then the missing complexity of the reaction mechanism will be substituted by the spatial complexity of the reaction−diffusion system

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and the complexity of the electric potential distribution in the new construction.

Semiconductor Transistor and Its Direct Ionic Analogue. Regarding the physical and chemical features assigned to the new amplifying device, our first guess was that a structure analogous to the well-known semiconductor transistor could satisfy our requirements. In this new transistor OH^- and H^+ ions could play the role of electrons and holes, respectively. It is known that there is a close analogy in the description of ion electrodiffusion[34] and the phenomenological theory of electron and hole transport in semiconductors. To facilitate the reading, we cite a brief semiconductor–ionics "vocabulary"[34] (used for the present problem):

holes	cations (here, H^+ ions)
electrons	anions (here, OH^- ions)
p-semiconductor	cation exchanger (here, in H form)
n-semiconductor	anion exchanger (here, in OH form)
diode	bipolar membrane diode[35] (two adjacent cation and anion exchange layers in H and OH form, respectively)
transistor	? (no experimental example)

What is remarkable in this vocabulary is that although a bipolar membrane diode was already reported 40 years ago,[35] no account of a membrane transistor has ever appeared. Obviously, there should be some technical problems hampering the progress in this direction. To understand this, first the working principle of the semiconductor transistor is recalled briefly. The original transistor[36,37] (npn or pnp) is a semiconductor device containing two n–p junctions that is two semiconductor diodes. If these junctions are close enough (that is, the middle zone: the so-called base layer is thin), then most of the majority carriers (electrons or holes) of the first layer (the so-called emitter) can diffuse through the thin base layer without recombination to the third layer of the transistor (the so-called collector). To satisfy this condition, the width of the base layer, e.g., in a pnp transistor, is usually around 1 μm, which is only one-tenth of the so-called diffusion length,[38] $L_p = 10\ \mu$m, of the holes in the base:

$$L_p = \sqrt{D_p \tau_p} \tag{1}$$

where $D_p = 10$ cm^2/s is the diffusion constant and $\tau_p = 10^{-7}$ s is the lifetime of the holes in the base. If the width of the base is much larger than 1 μm, then most of the holes injected from the emitter recombine in the base before reaching the base–collector junction. In this case, the transistor action is lost and the p–n–p structure becomes merely two diodes connected back to back.

Now let us see the requirements for a hypothetical membrane transistor of the H–OH–H type. Such a transistor would contain a thin layer of anion exchanger in OH form sandwiched between two layers of H form cation exchangers. In the active mode of the transistor, the forward-biased emitter would inject H^+ ions to the base. To observe transistor action, most of these H^+ ions should reach the reverse-biased base–collector junction without recombination. To determine the critical width of the base layer, first the diffusion length L_H of the H^+ ions in the base should be calculated:[39]

$$L_H = \sqrt{D_H \tau_H} \tag{2}$$

Here, $D_H = 9.32 \times 10^{-5}$ cm^2/s is the diffusion constant and $\tau_H = 1/(1.3 \times 10^{11})$ s is the lifetime of the H^+ ions in the base at 25 °C.[40] (The lifetime of H^+ ions was calculated assuming a 1 M OH^- ion concentration in the base, which is a usual concentration of fixed ions in an ion exchange membrane.[41]) The result is $L_H = 0.27$ nm, and to get good transistor action, the width of the base should be even 10 times smaller. Obviously, to make such a thin membrane is impossible, since its thickness should be in or below the atomic dimensions. Decreasing the concentration of the fixed groups in the base cannot help too much and would cause other problems. Thus, it can be concluded that a direct ionic analogue of the semiconductor transistor, the ion exchange membrane transistor, would be extremely difficult to realize experimentally, and this is why it was never constructed. This substantial difference is mainly due to the different recombination mechanisms. Although in semiconductors a direct recombination of holes and electrons is very unlikely and the recombination process occurs through intermediate-level states[37] (also called recombination centers), the direct recombination between H^+ and OH^- ions is a fast, diffusion-controlled reaction.[40]

Indirect Analogue: The Electrolyte Transistor. When it was understood that a direct ionic analogue of the classical transistor is not a viable candidate for an acid–base chemoelectric amplifier we turned to other possibilities and to less-close analogues. Since a transistor contains two diodes, we looked for other chemical diodes that could be combined to form a transistor more successfully. A natural first choice was the so-called electrolyte diode,[42,43] which was developed and studied in our laboratory. Such a diode is a hydrogel cylinder connecting aqueous solutions of a strong acid and base. The cylinder occupies a small hole cut into an electric insulator wall separating the above-mentioned aqueous solutions. The gel prevents any convective mixing of the liquids, but diffusion and ionic migration of small molecules and ions across the gel are possible. In the forward direction the alkaline solution (e.g., 0.1 M KOH) has a positive potential with respect to the acidic one (e.g., 0.1 M HCl). This polarity compels the cations from the base (K^+) and the anions from the acid (Cl^-) to migrate into the gel where they form a well conducting salt solution. When a reverse bias is applied, OH^- ions from the base and H^+ ions from the acid migrate into the gel and recombine. As all other ions are expelled from the acid–base boundary, a thin layer of electrolyte-free pure water, a depletion region with high impedance,[42,43] is formed this way. As a consequence, the current flowing through an electrolyte diode is much smaller for the reverse bias than for the forward one; that is, the device has a diode characteristic. On the other hand, the working principle of this diode is different from that of the semiconductor or the ion exchange diode. Both the semiconductor and the ionic bipolar membrane diode contain certain fixed ions. These are donor or acceptor ions fixed by the crystal lattice in a semiconductor and cations or anions bonded covalently to a polymer network in an ion exchange membrane diode. There are no fixed ions in our electrolyte diode, however. In the gel we have only ions that can move freely under the influence of electric potential or concentration gradients. As a result of the different working principles, recombination of holes and electrons in a semiconductor diode and recombination of H^+ and OH^- ions in a ion exchange diode occur in the forward direction, but in an electrolyte diode, recombination of hydrogen and hydroxyl ions proceeds when it is reversely biased.

Here, we report that two electrolyte diodes can be combined successfully to form an electrolyte transistor. A key element of the success is that in the new device all ions are mobile but only two of them, the hydrogen and the hydroxyl ions, can recombine. The other two, i.e., K^+ and Cl^- ions, cannot disappear in a chemical reaction, and consequently, they diffuse easily through the thin base layer without recombination. It will be shown, however, that the working principle, the concentration distributions, and the behavior of an electrolyte transistor are all more complex than can be expected from the previous simple considerations.

Finally, we emphasize that electrochemical reactions at the electrodes (which are placed far away from the electrolyte transistor) do not play any role here. Thus, the working principle of our device is different from the microelectrochemical transistor developed by Wrigthon and co-workers[44−46] and other devices based on various electrochemical reactions.[46]

Experimental Section

Materials. Poly(vinyl alcohol) (nominal molecular weight of 15 000, Fluka), glutardialdehyde (25% aqueous solution, grade I, Sigma), Cab-O-Sil fumed silica (grade H-5, Cabot Corp.), *n*-hexane (Reanal), and silicon rubber tubing (Pemü) were used as received. Solutions of 0.1 M KOH and HCl were prepared of reagent grade chemicals (Reanal) with doubly distilled water.

Gel Recipe. A quantity of 0.2 g Cab-O-Sil was thoroughly mixed with 2 mL of distilled water and with 1 mL glutardialdehyde solution (2% diluted from the stock). The mixture was degassed to prevent bubble formation in the later steps of the procedure. Then 4 g poly(vinyl alcohol) solution (28.7% w/w) was added, and the mixture was homogenized by stirring with a glass rod. Finally, 1 mL of 5 M HCl was added under continuous stirring. Since the gelling of this mixture is rather quick, it was used immediately to prepare gel cylinders. The role of the fumed silica applied in the recipe is to improve the mechanical strength and the stability of the gel.

Preparation of Gel Cylinders. A part of the freshly prepared mixture was poured into a 5 mL plastic syringe, and with the aid of the syringe, silicon rubber tubings (inner diameter of 1 mm, outer diameter of 3 mm, length of 40−50 mm) were filled. After 30 min the gel was set, and the silicon tubings with the gel cylinders inside were placed under *n*-hexane where the silicon tubing expanded considerably. To remove a gel cylinder from a tubing, a syringe filled with hexane was attached to the tubing. Then, pressing the syringe forced the hexane to flow through the swollen tubing, and the gel cylinder slipped out simultaneously. The gel cylinders were washed with water, placed in 1 M KOH for 1 h, and stored in distilled water afterward.

Results and Discussion

Transistor Action in the Acid−Base−Acid Electrolyte Transistor. An electrolyte transistor can be constructed from two electrolyte diodes in a way similar to its semiconductor counterpart. 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 a hydrogel cylinder (diameter of 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) Plexiglas walls with holes for the gel (Figure 1). 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 the fresh electrolyte solutions is applied. The middle compartment is narrow; the distance between the two Plexiglas 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 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. The transistor action was demonstrated first with an SLS transistor in the "common base" configuration (Figure 1). Some characteristics of the transistor are shown in Figures 2 and 3.

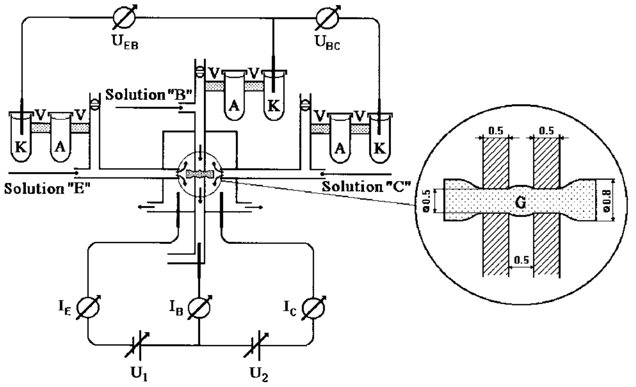

Figure 1. Schematic drawing of the apparatus used for the electrolyte transistor measurements. The insert shows the most important part: the swollen gel cylinder "G" and its surroundings. The cylinder was partially dried to make it thinner before it was inserted into the two 0.5 mm diameter holes drilled into the two parallel 0.5 mm thick Plexiglas walls. When the thin and dry gel was placed in its final position, it was fixed there by swelling with water. The 0.5 mm thick channel between the two walls has a rectangular cross-section (0.5 mm × 5 mm). Thus, solution "B" (the electrolyte in contact with the base of the transistor) can flow freely around the central part of the gel. "E" and "C" are electrolyte solutions for the emitter and the collector. There are six electrodes in the apparatus: three platinum electrodes for the current and three Ag/AgCl electrodes for the voltage measurements. The Ag/AgCl electrodes were connected through a special salt bridge system to decrease liquid junction potentials. V: Vycor porous glass. A: 10 M NH_4NO_3. K: 1 M KCl solutions. Peristaltic pumps, reservoirs and their accessories are not shown here. U_1 and U_2 are variable voltage sources (HP E3612A). The U_{EB}, U_{BC} voltage and the I_E, I_B, I_C current meters could be connected to a 486 compatible PC via a PC−Lab card PCL-711S. Data were collected by the Labtech Notebook program.

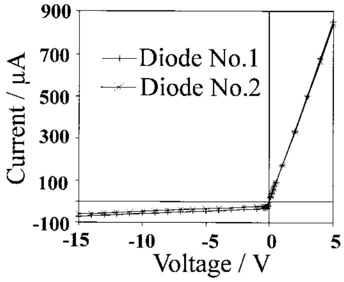

Figure 2. Current−voltage characteristics of the two diodes in the SLS transistor. Sign convention: currents and voltages are taken as positive in the forward direction. (In the case of acidic−alkaline interfaces a positive current is flowing from the alkaline region toward the acidic one. A voltage between acidic and alkaline zones is positive if the alkaline zone has a more positive potential.) Because relaxation time constants of the measurements were between 2 and 4 s, all steady-state currents were recorded only after 20 s.

Figure 2 displays the current−voltage characteristics of the two diodes of the transistor when they are connected in parallel. In this case both diode characteristics are similar to that of a single diode and there is no interaction between them. If both diodes are reversely biased (this is the "cutoff mode" of the

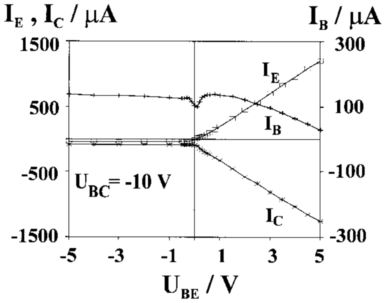

Figure 3. Demonstration of the transistor action in the common-base configuration. (Note the different scales for the various currents.) Without this action the current flowing through the collector-base diode would depend on the collector-base voltage only and would not change if that voltage was kept constant. The curves prove, however, that in the active mode the collector current is also affected by the base-emitter voltage and grows parallel with the increasing emitter current. The sign convention is the same as in Figure 2; emitter and collector currents are taken as positive when they flow out from the SLS transistor. The same sign convention is applied to the base current.

transistor), the current is small, increases somewhat with the voltage, and also has a voltage-independent component. In the forward direction ("saturation mode" of the transistor) the current is larger and proportional to the voltage.

Figure 3 demonstrates the transistor action. One of the diodes was chosen as the "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 emitter, base, and collector currents (I_E, I_B, I_C) were measured as a function of this variable. When the base-emitter 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). This experiment clearly proves a transistor action, but a thorough understanding of this action based on the ionic currents requires further discussion.

Ionic Currents in the SLS Transistor. Our aim here is to find a qualitative explanation for the transistor characteristics shown in Figure 3. Figure 4 displays three qualitatively different pictures of the component currents as U_{BE} is increased from negative to positive in Figure 3.

Figure 4a shows the ionic and electric currents when both diodes are reversely biased. In this Figure, $|U_{BE}| < |U_{BC}|$; consequently, $|I_E| < |I_C|$. Since the applied reverse bias prevents the migration of the K^+ and Cl^- ions, the electric current is carried exclusively by the H^+ ions in the acidic regions and by the OH^- ions in the alkaline regions. Thus, the following simple relationships hold between the electric and ionic currents

$$I_E = j_E^H, \quad I_B = -j_B^{OH}, \quad I_C = j_C^H$$

where j_E^H and j_C^H is the hydrogen ion current in the emitter and in the collector, respectively, and j_B^{OH} is the hydroxyl ion current in the base. (For the sake of simplicity the Faraday number is 1 here.) A current is represented by an arrow, the length of which is proportional to its absolute value. The acidic and alkaline regions are separated by thin recombination zones marked by vertical lines. The potential drops U_{BE} and U_{BC} are concentrated mainly to these zones. Now, if we regard the trends of the various currents in the $-5\text{ V} < U_{BE} < 0\text{ V}$ interval in Figure 3, these can be explained qualitatively on the basis of Figure 4a. First, because U_{BC} is kept constant, I_C should be independent of U_{BE} in this interval. Second, $|I_E|$ should follow the reverse-biased diode characteristic in this interval; it decreases slowly with the decreasing negative bias and drops sharply when U_{BE} is close to zero. These predictions are in good agreement with the experimental curves. Because $I_B = -(I_E + I_C)$, the predicted trends can be observed in the base current as well.

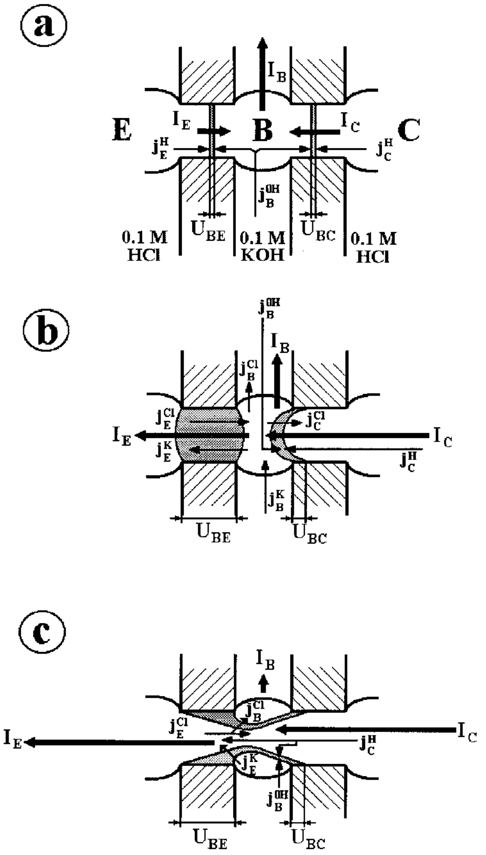

Figure 4. Electric and ionic currents in the SLS transistor: (a) currents in the cutoff mode in which both diodes are reversely biased; (b) active mode at low base-emitter voltages ($U_{BE} = 0.1-0.3$ V) (c) active mode and acidic tunnel formation at higher base-emitter voltages ($U_{BE} > 1$ V).

Figure 4b shows a situation where the emitter-base diode is biased slightly ($0.1\text{ V} < U_{BE} < 0.3\text{ V}$) in the positive (forward) direction. In this case Cl^- ions from the emitter and K^+ ions from the base are driven to the emitter-base boundary where they form a KCl solution. This "salt zone", where the acid or base concentration is negligible compared with that of the salt, is much wider than the previous recombination zone. In steady state

$$j_E^K \approx -j_E^{Cl}$$

where j_E^K and j_E^{Cl} is the current of the potassium and the chloride ions, respectively, in the emitter region. This is because the concentration and the ionic mobility of these two ions are roughly equal in the salt zone and the ionic currents in this zone are driven mainly by the potential and not by the concentration gradients.[47] A similar relationship holds between the current of the hydrogen and chloride ions in the collector region:

$$j_C^H \approx -5j_C^{Cl}$$

because the concentration of the two ions are roughly equal[48] in the recombination zone between the base and the collector, but the mobility of H^+ ions is about 5 times larger than that of the Cl^- ions. The only parameter that is difficult to estimate is the ratio α:

$$\alpha = \frac{j_{\mathrm{C}}^{\mathrm{Cl}}}{j_{\mathrm{E}}^{\mathrm{Cl}}}$$

If the electric field is negligible inside the base, then α is determined by geometrical conditions. In Figure 4b it was assumed that about half of the chloride ions crossing the salt zone will leave the transistor across the collector and the other half across the base, that is $\alpha = 0.5$. (Most probably, α is higher than 0.5 because the electric field can penetrate at least partially into the base region, forcing most of the chloride ions toward the collector. Thus, especially at higher collector currents, α should be around 1.) Now the currents can be expressed as a function of α and i, $i \equiv |j_{\mathrm{E}}^{\mathrm{Cl}}|$:

$$I_{\mathrm{E}} = 2i, \quad I_{\mathrm{C}} = -6\alpha i, \quad I_{\mathrm{B}} = (6\alpha - 2)i$$

Moreover, because i should be proportional to the base-emitter voltage

$$i \sim U_{\mathrm{BE}}$$

all currents should grow in absolute value as we increase U_{BE}. Comparing this theory with the characteristics in Figure 3, we can see that the prediction is correct at small voltages but I_{B} fails to grow further around 0.5 V and even starts to decrease above 1 V. This contradicts Figure 4b especially because α can only grow with the increasing currents, and this effect should enhance I_{B} further. The only possibility is that the qualitative picture of the concentration and ionic current distributions within the transistor change drastically at these higher voltages. This qualitatively new situation is shown in Figure 4c.

Figure 4c displays ionic currents in the SLS transistor when U_{BE} is above 1 V. A most characteristic feature of this picture is an acidic tunnel across the alkaline middle region of the transistor. The tunnel connects the emitter and the collector, and its "wall" separates the acidic and alkaline regions. This wall, however, is neither a pure recombination nor a salt zone because the potential difference is not constant across it. Because of the current flowing in the tunnel, there is an ohmic voltage drop along the wall. As a result, wall areas close to the emitter are salt zones where the acid−base interface is forward-biased while other parts of the wall are recombination zones where the acid−base interface is reverse-biased. This qualitative picture is in agreement with the characteristics of Figure 3 measured above 1 V. First, it is easy to understand why the absolute values of I_{E} and I_{C} are so close to each other and grow in parallel. This is because most of the hydrogen and chloride ion current flows inside the tunnel between the emitter and the collector and ionic currents flowing across the wall are much smaller. Second, the negative slope of the base current can be also explained. At low U_{BE} values the reverse current of the recombination zones, which is regarded to be positive according to our sign convention in the SLS transistor, dominates. Increasing U_{BE} increases the salt regions of the wall together with the forward current (regarded to be negative) flowing in those regions while the area of recombination zones and their positive contribution to the base current decreases. These effects explain the decrease of I_{B} with increasing U_{BE}.

Common Emitter Current Gain. Usually, transistors are applied for amplification in the common emitter configuration. Such characteristics of the electrolyte transistor are shown in Figure 5. From these characteristics β_0, the common emitter current gain, can be calculated in the usual way:

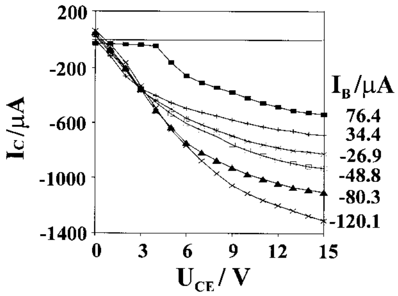

Figure 5. Output characteristics of the SLS transistor in the common emitter configuration.

$$\beta_0 \equiv \frac{\Delta I_{\mathrm{C}}}{\Delta I_{\mathrm{B}}} \approx 4-5$$

Changing the roles of the emitter-base and the collector-base diodes (inverted mode of operation) made no difference in our experiments because the two diodes were symmetrical here. Varying the electrolyte concentrations, however, could easily break this symmetry, and such asymmetric transistors are planned to be studied in the future.

Properties of the LSL Transistor. The complement of the SLS transistor is the LSL transistor. Cutoff and saturation mode characteristics of this transistor are similar to that of the SLS transistor. In the active mode, however, above a certain U_{EB} voltage the LSL transistor is unstable and exhibits complex oscillations. In Figure 6 the collector current is shown as a function of time at fixed $U_{\mathrm{CB}} = -10$ V for different emitter-base voltages (base configuration). Like in the case of membrane oscillators[30,31] or the filament transistor[36] the source of the instability is, in a certain sense, a bistable behavior. As an experimental evidence for this bistability, a hysteresis curve was measured on an LSL transistor whose acidic feedstream was contaminated with KCl (0.1 M KOH, 0.1 M HCl + 0.15 M KCl, 0.1 M KOH). In Figure 7 the collector current of this transistor is shown as a function of the emitter-base voltage. Owing to the contaminated feedstream, the K^+ concentration in the base is 0.15 M even at negative emitter voltages. This K^+ concentration increases further, however, at positive emitter voltages (there is a transport of K^+ ions from the emitter to the base due to the emitter current), and at a critical voltage (this means a critical K^+ concentration in the base) the collector current jumps to a higher value. Most probably, this higher current indicates the formation of an alkaline tunnel across the middle acidic part of the LSL transistor similar to the acidic tunnel of the SLS transistor. Bistability occurs if that tunnel can survive at emitter voltages that are lower than the critical one. This creates hysteresis, and the collector current jumps back to its original branch only at a lower emitter voltage.

Now the oscillations in the uncontaminated transistor can be explained qualitatively on the basis of the former bistable behavior. First, the collector current is small because the K^+ concentration is below a critical level in the base. However, owing to the emitter current, the K^+ concentration in the base gradually increases and finally reaches its critical value. At this point the collector current jumps to a more negative value. Because of this high collector current, however, the K^+ concentration now starts to decrease rapidly in the base (since the feedstream of the base contains no K^+ ions in this case), and at a lower critical value the collector current jumps back to its original level and the cycle starts again. It is clear, however, that this simple theory does not explain the complex character of the oscillations. The most fundamental problem is, however,

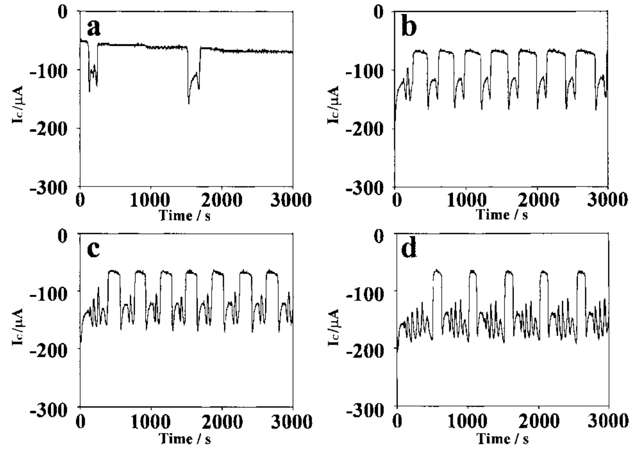

Figure 6. Excitability and oscillations in the active mode of the LSL transistor. Common base configuration is with $U_{CB} = -10$ V. Collector current is shown as a function of time at (a) $U_{EB} = 1.2$ and 1.3 V. There are no oscillations, but the transistor is excitable. This means that the steady state is stable but perturbations can generate a "single peak" response. The first peak appeared when U_{EB} was increased stepwise from 1.1 to 1.2 V. The second one was generated by the next increase from 1.2 to 1.3 V. Complex oscillations at $U_{EB} =$ (b) 1.4 V, (c) 1.5 V, (d) 1.7 V. The oscillations exhibit a regular pattern except for a transient period at the beginning. The time period and the average current grow with increasing voltage.

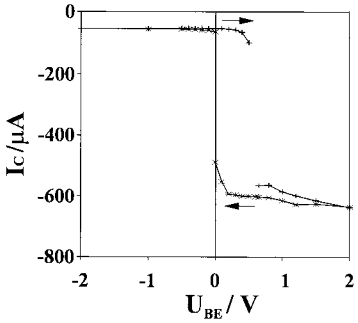

Figure 7. Hysteresis and bistability in the active mode of an LSL transistor, the base of which is contaminated with KCl. $U_{BC} = -2$ V.

to understand the qualitatively different behavior of the SLS and LSL transistors, that is, to find a mechanism creating bistability in the latter but not in the former one. Some unspecified negative charges in the gel[43] can explain this, but further experiments are needed to check this suggestion.

Conclusions, Applications, and Connections to Other Complex Systems

We have constructed a new chemical device that works in many respects like a transistor and can amplify electric signals in a similar way. Although this is an interesting property, the transducer function of the electrolyte transistor is probably a more important feature in possible applications. Electric voltage in the first diode controls the concentration distributions in the base of the transistor and consequently the ion migration from the base toward the depletion zone of the second diode, and this way affects the electric current there. Thus, in our chemical transistor the first diode transforms an electric signal to a chemical one and in the second diode this chemical signal is transformed back to an electric one again. Control and amplification of chemical concentration changes would be a natural application of the new device, and such possibilities are under investigation in our laboratory.

Complex oscillations and related dynamical phenomena displayed by the acid−base−acid transistor are also worth further experimental and theoretical studies especially because these are complex oscillations of spatiotemporal patterns.[49,50]

Regarding biological analogies, it is worth mentioning that simultaneous electric and pH gradients can be found in the mitochondrial inner membrane and the thylakoid membrane of the Chloroplast,[51] and these gradients play an important role in the chemiosmotic ATP synthesis. Although the H^+ ion concentration difference (about 1 pH unit) and the electric potential difference (about 100 mV reverse-biased) are much smaller across real biological membranes than in our experiments, the gradients can be comparable because the biomembranes are much thinner. Thus, a size reduction of the electrolyte diode and the transistor would be desirable to approach the dimensions of the biomembranes and also to obtain faster devices.

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References and Notes

(1) *Dynamism and Regulation in Nonlinear Chemical Systems* (*Physica D84*); Marek, M. A., Müller, S. C., Yamaguchi, T., Yoshikawa, K. Eds.; North-Holland: Amsterdam, 1995.

(2) Nicolis, G.; Prigogine, I. *Exploring Complexity*; Freeman: New York, 1989.

(3) Bar-Yam, Y. *Dynamics of Complex Systems*; Addison-Wesley: New York, 1997.

(4) Zhabotinsky, A. M. *Biofizika* **1964**, *9*, 306.

(5) Field, R. J., Kõrös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1974**, *94*, 8649.

(6) Field, R. J., Burger, M., Eds. *Oscillations and Traveling Waves in Chemical Systems*; Wiley: New York, 1985.

(7) Scott, S. K. *Oscillations, Waves, and Chaos in Chemical Kinetics*; Oxford University Press: Oxford, 1994.

(8) Zaikin, A. N.; Zhabotinsky, A. M. *Nature* **1970**, *225*, 535.

(9) Winfree, A. T. *Sci. Am.* **1974**, *230*, 82.

(10) De Kepper, P.; Boissonade, J. From Bistability to Sustained Oscillations in Homogeneous Chemical Systems in Flow Reactor Mode. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985; Chapter 7.

(11) Epstein, I. R.; Orbán, M. Halogen−Based Oscillators in a Flow Reactor. Chapter 8.

(12) Noszticzius, Z.; Horsthemke, W.; McCormick, W. D.; Swinney, H. L.; Tam, W. Y. *Nature* **1987**, *329*, 619.

(13) Tam, W. Y.; Horsthemke, W.; Noszticzius, Z.; Swinney, H. L. *J. Chem. Phys.* **1988**, *88*, 3395.

(14) Kshirsagar, G.; Noszticzius, Z.; McCormick, W. D.; Swinney, H. L. *Physica D* **1991**, *49*, 5.

(15) Castets, V.; Dulos, E.; Boissonade, J.; De Kepper, P. *Phys. Rev. Lett.* **1990**, *64*, 2953.

(16) Ouyang, Q.; Swinney, H. L. *Nature* **1991**, *352*, 610.

(17) Kapral, R., Showalter, K., Eds. *Chemical Waves and Patterns*; Kluwer: Dordrecht, The Netherlands, 1995.

(18) Johnson, B. R., Scott, S. K. *Chem. Soc. Rev.* **1996**, 265.

(19) Winston, D.; Arora, M.; Maselko, J.; Gáspár, V.; Showalter, K. *Nature* **1991**, *351*, 132.

(20) Lázár, A.; Noszticzius, Z.; Försterling, H. D.; Nagy-Ungvárai, Zs. *Physica D* **1995**, *84*, 112.

(21) Lázár, A.; Noszticzius, Z.; Farkas, H.; Försterling, H. D. *Chaos* **1995**, *5*, 443.

(22) Steinbock, O.; Kettunen, P.; Showalter, K. *Science* **1995**, *269*, 1857.

(23) Lázár, A.; Försterling, H. D.; Volford, A.; Noszticzius, Z. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2903.

(24) Lázár, A.; Försterling, H. D.; Farkas, H.; Simon, P.; Volford, A.; Noszticzius, Z. *CHAOS* **1997**, *7*, 731.

(25) Marlovits, G.; Wittmann, M.; Noszticzius, Z.; Gáspár, V. *J. Phys. Chem.* **1995**, *99*, 5359.

(26) Volford, A.; Wittmann, M.; Marlovits, G.; Noszticzius, Z.; Gáspár, V. *J. Phys. Chem. B.* **1997**, *101*, 3720.

(27) Agladze, K.; Aliev, R. R.; Yamaguchi, T.; Yoshikawa, K. *J. Phys. Chem.* **1996**, *100*, 13895.

(28) Steinbock, O.; Kettunen, P.; Showalter, K. *J. Phys. Chem.* **1996**, *100*, 18970.

(29) Winfree, A. T. *Chaos* **1991**, *1*, 303.

(30) Larter, R. *Chem. Rev.* **1990**, *90*, 355.

(31) Kim, J. T.; Larter, R. *J. Phys. Chem.* **1991**, *95*, 7948.

(32) Rábai, Gy.; Orbán, M.; Epstein, I. R. *Acc. Chem. Res.* **1990**, *23*, 258.

(33) Rábai, Gy. *J. Phys. Chem. A* **1997**, *106*, 7085.

(34) Rubinstein, I. *Electro-Diffusion of Ions*; SIAM Studies in Applied Mathematics 11: SIAM: Philadelphia, 1990.

(35) Lovrecek, B.; Depsic, A.; Bockris, J. O'M. *J. Phys. Chem.* **1959**, *63*, 750.

(36) Shockley, W. *Electrons and Holes in Semiconductors*; Van Nostrand: New York, 1950.

(37) Sze, S. M. *Semiconductor Devices. Physics and Technology*; Wiley: New York, 1985.

(38) The minority carrier distribution (in this case the concentration profile of the holes) in the neutral base region can be described by the field-free steady-state continuity equation (p 115 in ref 37):

$$D_p\left(\frac{d^2p_n}{dx^2}\right) - \frac{p_n - p_n^E}{\tau_p} = 0$$

where p_n is the minority carrier concentration, p_n^E is its equilibrium value, and D_p and τ_p are the diffusion constant and the lifetime of the holes, all in the n-doped base layer. The general solution of the above differential equation

$$p_n(x) = p_n^E + C_1 \exp\left(\frac{x}{L_p}\right) + C_2 \exp\left(-\frac{x}{L_p}\right)$$

where $L_p = (D_p\tau_p)^{1/2}$ is the diffusion length of the holes and C_1 and C_2 are constants determined by the boundary conditions. In a good transistor, where the width of the base is only 10% of the diffusion length, the calculated concentration profile is close to a straight line connecting the given boundary values.

(39) The steady-state continuity equation for hydrogen ions diffusing through a thin OH form anion exchanger membrane can be written in the following form:

$$D_H\left(\frac{d^2c_H}{dx^2}\right) - k_r c_{OH}\left(c_H - \frac{K_W}{c_{OH}}\right) = 0$$

where c_H and c_{OH} are the hydrogen and hydroxyl ion concentrations, $k_r = 1.3 \times 10^{11}$ M^{-1} s^{-1} is the rate constant of the recombination reaction, and K_W is the ionic product of water. We can introduce the following notations

$$\tau_H \equiv (k_r c_{OH})^{-1}, \quad c_H^E \equiv \frac{K_W}{c_{OH}}$$

and with the help of these new parameters a differential equation analogous to the one given in ref 38 can be obtained:

$$D_H\left(\frac{d^2c_H}{dx^2}\right) - \frac{c_H - c_H^E}{\tau_H} = 0$$

The solution of this equation can be also given in a similar form where $L_H = (D_H\tau_H)^{1/2}$ is the diffusion length of the hydrogen ions.

(40) Strehlow, H.; Knoche, W. *Fundamentals of Chemical Relaxation*; Monographs in Modern Chemistry; Verlag Chemie: Weinheim, New York 1977.

(41) Simon, G. P. *Ion Exchange Training Manual*; Van Nostrand Reinhold: New York 1991.

(42) Hegedus, L.; Noszticzius, Z.; Papp, Á.; Schubert, A.; Wittmann, M. *ACH−Models Chem.* **1995**, *132*, 207.

(43) Hegedus, L.; Wittmann, M.; Kirschner, N.; Noszticzius, Z. *Prog. Colloid Polym. Sci.* **1996**, *102*, 101.

(44) White, H. M.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375.

(45) Thackeray, J. W.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 5133.

(46) Wrighton, M. S. *Science*, **1986**, *231*, 32.

(47) According to the one-dimensional Nernst−Planck equations the current density of an ion is a sum of two terms

$$j = j(\Delta c) + j(\Delta\varphi)$$

where the first term is due to the diffusion generated by the concentration gradients or differences

$$|j(\Delta c)| = D\frac{dc}{dx} \approx D\frac{\Delta c}{\Delta x}$$

and the second term is due to the ionic migration caused by the electric potential gradients

$$|j(\Delta\varphi)| = Dc\cdot\frac{zF}{RT}\frac{d\varphi}{dx} \approx Dc\cdot\frac{1}{25.6\text{ mV}}\frac{\Delta\varphi}{\Delta x}$$

Assuming that the concentration difference and the concentration are close, we can approximate the ratio of the two terms as

$$\frac{|j(\Delta c)|}{|j(\Delta\varphi)|} \approx \frac{25.6\text{ mV}}{\Delta\varphi}$$

From this result, we can see that if $\Delta\varphi = 0.1$ V the contribution of diffusion to the total ionic current is around 20% only and for higher voltages it can be negligible.

(48) The approximation holds only when the concentrations of the hydroxyl and any other anions in the depletion zone are negligible compared with that of the contaminating chloride ions there.

(49) Petrov, V.; Ouyang, Q.; Swinney, H. L. *Nature* **1997**, *388*, 655.

(50) Walgraef, D. *Spatio-Temporal Pattern Formation*; Springer: New York, 1997.

(51) Cooper, G. M. *The Cell*; ASM Press & Oxford University Press: Oxford, 1997.