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Toward complementary ionic circuits: the *npn* Ion Bipolar Junction Transistor

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Abstract: Many biomolecules are charged and may therefore be transported with ionic currents. As a step towards addressable ionic delivery circuits, we report on the development of a *npn* Ion Bipolar Junction Transistor (*npn*-IBJT) as an active control element of anionic currents in general, and specifically, demonstrate actively modulated delivery of the neurotransmitter glutamic acid. The functional materials of this transistor are ion exchange layers and conjugated polymers. The *npn*-IBJT shows stable transistor characteristics over extensive time of operation and ion current switch times below 10 s. Our results promise complementary chemical circuits similar to the electronic equivalence, which has proven invaluable in conventional electronic applications.

Electrophoretic delivery of ions and charged biomolecules is attractive since it induces little convection, does not rely on moving mechanical parts and the delivered amount of substance can be correlated to the electric current¹⁻². Delivery rate and temporal control can be mediated through the applied voltage. However, in order to achieve more advanced features, such as addressability in a delivery matrix circuits, active components that exhibits non-linear device characteristics are needed. In conventional electronics these components are often diodes and transistors³. Diodes are two terminal devices with the property of current rectification while transistors generally are three terminal devices in which the current between two terminals can be modulated and amplified by a third terminal. In order to mimic electronic circuits and construct ionic circuits, in which ions and charged biomolecules are transported, ionic transistors and diodes must be developed. Ideally, these ionic transistors should have a high ratio between the on and off current to minimize leakage, a fast switching speed, a high current gain, be possible to integrate into a larger system and they should also be functional at physiological conditions. Recently, nanofluidic transistors and diodes have received a lot of attention⁴⁻⁶. In these devices the surface charge along the walls of the thin channels modulates the conductivity through the device. Although these devices show diode- and transistor-like behavior they are typically only functional at relatively low salt concentrations as the Debye screening length at 100 mM is ~ 1 nm. Other routes for constructing ionic transistors have been explored but without successful operation at physiological conditions⁷.

An alternative approach to achieve ionic transistors is to utilize ion exchange membranes⁸. These membranes contain fixed ionic groups which are compensated by mobile ions of the opposite charge (counter-ions). The electrostatic repulsion (Donnan exclusion) of mobile ions of the same charge (co-ions) as the fixed groups renders the membrane selective to the counter-ions, even at physiological conditions⁸. Cation- and anion-selective

membranes are in many aspects the ionic equivalent to *p*- and *n*-doped semiconductors, respectively. By sandwiching a cation- and an anion-selective membrane a bipolar membrane (BM) is obtained⁹⁻¹⁰. BMs exhibit current rectification in similarity to bipolar semiconductor pn-junction diodes. The rectification is caused by depletion and enrichment of mobile ions in between the membranes at reverse and forward bias, respectively. BMs are used in a variety of applications¹¹, e.g. in electrodialytic water splitting, and more recently as diodes in ionic circuits¹². However, addressing circuits entirely composed of diodes exhibit severe limitations and its use in conventional electronics is limited.

Figure 1. The *npn*-IBJT biased in the common-emitter configuration. (A) The emitter and collector are separated from the base by a neutral polymer electrolyte. Conductive PEDOT:PSS electrodes covered by electrolytes inject/extract ions to/from the terminals of the transistor. (B) In the active mode the base supplies the junction with cations. (C) In the cutoff mode the base depletes the junction of mobile cations. (D) The junction is formed by an opening in the SU-8 insulation layers which is filled with a polymer electrolyte. The distance between the emitter and collector is 100 μm .

To go beyond the limitations of diode-based ionic circuits we recently reported an Ion Bipolar Junction Transistor (IBJT)¹³. This ionic transistor was of the *pnp*-type and can modulate the transport of cations at physiological conditions. Here we report on the development of the complementary version of this device, the *npn*-IBJT (Figure 1). The characteristics of the device are

presented along with a demonstration of modulated transport of the biologically relevant neurotransmitter glutamic acid. Not only does this device allow for regulation of anionic currents, but in combination with the *pnp*-IBJT it enables construction of complementary circuits, which has proven very fruitful in the conventional electronics industry¹⁴.

The *nnp*-IBJT consists of anion-selective emitter and collector, cation-selective base and a neutral polymer electrolyte junction (Figure 1). The device can be seen as two BMs (emitter-base (E-B) and collector-base (C-B)) which share the same base and junction. A thin film of the conductive polymer¹⁵⁻¹⁶ poly(3,4-ethylenedioxythiophene)¹⁷ doped with the polyanion poly(styrenesulfonate) (PEDOT:PSS) coated on a plastic (PET) foil is used as substrate. The cation-selective base comprises over-oxidized¹⁸ PEDOT:PSS, *i.e.* leaving PSS ionically conductive and PEDOT electronically non-conducting. Two 10 μm thick insulating layers of SU-8 are deposited on top of the PEDOT:PSS pattern with openings located at the electrodes and at the junction (Figure 1D). The emitter and collector are patterned between the two SU-8 layers and are in contact with the neutral poly(ethylene glycol) (PEG) electrolyte (Figures 1B-D). The anion-selective layer is ~ 700 nm thick and consists of poly(vinylbenzylchloride) partly quaternized by N-benzyltrimethylamine (labeled q-PVBC, Figure 1) and crosslinked with 1,4-diazabicyclo[2.2.2]octane. The junction is covered by a polydimethylsiloxane (PDMS) layer to encapsulate the polymer electrolyte.

Figure 2. Schematic drawings of concentrations and electric potentials. (A) The concentration of fix charges (X_N) is much higher than the electrolyte concentration (c_0), thereby excluding cations from the membrane. In the active mode a linear diffusion gradient is created inside the junction. (B) In the cutoff mode the whole potential drop occurs at the junction-collector interface. In the active mode there are resistive potential drops (ΔV_E) inside the emitter and collector.

Electric currents are translated into ionic ones at the patterned PEDOT:PSS electrodes¹⁹, which in part are covered by aqueous electrolytes, according to the electrochemical reaction $\text{PEDOT}^+:\text{PSS}^- + \text{M}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{PEDOT}^0 + \text{M}^+:\text{PSS}^-$. The common-emitter transistor configuration (Figure 1A) was used throughout this work. When the electric potential at the base is lower than the potential at the emitter and collector ($V_{EB} < 0$) the transistor is in cutoff mode (Figure 1C). In this mode the base depletes the junction of cations, thus lowering the ion concentration in the bulk of the junction (c_J) which results in a low collector current (I_C) (Figure 2A). In the cutoff mode both the E-B and the C-B diodes are reversely biased. When increasing the

potential of the base so only the E-B diode is in forward bias ($0 < V_{EB} < V_{EC}/2$), the transistor operates in the active mode (Figure 1B). Cations are injected from the base and compensated by anions, primarily from the emitter, thus increasing c_J and correspondingly I_C . The resistive potential drop over the emitter (ΔV_E , Figure 2B) increases along with I_C and causes the potential drop across the E-B junction to decrease until the base current (I_B) equals the E-B leakage current, *i.e.* steady state. As I_B is small at steady state and ΔV_E equals V_{EB} , I_C is expected to depend linearly on V_{EB} : $I_C = R_E \cdot (V_{EB} - V_T)$ where V_T is the threshold voltage.

Insights into the active mode transport processes occurring inside the junction can be gained from the theory of over-limiting currents for ion exchange membranes²⁰. According to this theory a linear diffusion gradient is created from the emitter to collector within the bulk of the junction with I_C proportional to Δc_J (Figure 2A). At the J-C interface an extended space charge layer is formed with a high electric field which accounts for most of the potential drop within the junction²⁰⁻²¹. In the cutoff mode I_C is negligible and the entire potential drop occurs at the J-C interface. When V_{EB} approaches $V_{EC}/2$ the potential drop between E-B in the junction vanishes and the transistor operation turns into the so-called saturation mode. In this mode I_B is high and causes ion accumulation within the junction, resulting in a failure of membrane selectivity due to high salt concentrations.

Figure 3. Diode and switching characteristics. (A) The emitter-base diode shows current rectification with a linear slope in the forward direction due to the resistive load of the emitter and base channels. (B) The switching transients for a voltage step in V_{EB} from -3 V to 3 V. The 90% rise and 10% fall times are 9 s and 3 s, respectively.

Characterization was performed with aqueous 0.1 M NaCl electrolytes at all electrodes. A prerequisite for good transistor functionality is that the diodes work properly. Therefore, the E-B diode was characterized separately by disconnecting V_{EC} and scanning V_{EB} from -3 V to 3 V (15 mV/s) (Figure 3A). The measured current rectification ratio $|I_B(3 \text{ V})/I_B(-3 \text{ V})|$ was 55; comparable to previously reported rectification ratios for BMs²². I_B remains low at reverse bias which means that no pronounced field-enhanced water dissociation occurs. The transistor response

when switching between active and cutoff mode is of great interest. These current transients were measured by applying a voltage step to V_{EB} from -3 V to 3 V while keeping $V_{EC} = 10$ V (Figure 3B). When switched on, I_B is initially high but stabilizes quickly as I_C rises and reaches steady state. When V_{EB} is turned off, I_B depletes the junction of mobile cations, causing a fast decrease in I_C . The 90% rise time of I_C is 9 s and the 10% fall time is 3 s. The on-off ratio of the shown component was 30, however on-off ratios above 100 has been achieved for other components. Static transistor characteristics are useful for incorporating transistors into circuits. The transfer curve was obtained by scanning V_{EB} back and forth between -2 V and 3 V (2.5 mV/s) while keeping $V_{EC} = 10$ V (Figure 4A). As predicted I_C increases linearly versus V_{EB} in the active mode and is low in the cutoff mode ($V_{EB} < V_T = -0.2$ V). Advantageously, only minor hysteresis was present and I_B remained low throughout the whole scan. Further, the current-voltage output characteristics were obtained for different fixed values of V_{EB} by ramping V_{EC} (3 mV/s) in the active mode (Figure 4B). I_C is predicted to show saturation behavior with respect to V_{EC} , which also is measured in our devices. Finally the *nnp*-IBJT was characterized with floating base (Figure 4C). While in the cutoff mode, the base was disconnected and it was found that larger V_{EC} gave faster increase in and higher I_C . When 10 mol % NaOH was mixed into the emitter electrolyte I_C reached a significantly lower value. The floating base current can be attributed to a build up of c_J due to a small amount of water dissociation in the space charge layer at the collector interface. When hydroxide ions are transported from the emitter into the junction the proton concentration decreases together with I_C .

Figure 4. Transistor characteristics. (A) The transfer curve (I_C) is linear for higher V_{EB} and has little hysteresis. I_B remains low during the entire scan. (B) The output characteristics reveal saturation behavior in the active mode. The saturation mode was avoided due to high base currents. (C) I_C upon switch from the cutoff mode to floating base. A basic emitter electrolyte limits I_C due to recombination of protons and hydroxide ions inside the junction.

We have recently shown that organic conducting materials can be used *in vitro* and *in vivo* to translate electric signals into precise delivery of positively charged chemical messengers^{2,23-24}. To evaluate if the present *nnp*-IBJT can be used in a corresponding manner, *i.e.* as an addressable delivery point for negatively charged biomolecules, the transport of the neurotransmitter glutamic acid (Glu) was studied. The emitter electrode comprised 0.05 M Glu and 0.05 M NaCl whereas the collector electrolyte was loaded with an enzymatic detection kit for Glu. The color change at 40 μ m from the outlet was recorded by a microscope and analyzed. The normalized extracted color change in the green channel can be seen in Figure 5 as the *nnp*-IBJT is switched on and off by changing V_{EB} . Immediately after switching on, the Glu delivery starts and the corresponding color change is visible. After turning off the *nnp*-IBJT, the actual delivery stops and the released Glu molecules starts to diffuse away, resulting in a decrease of absorption intensity of the detection dye. This shows that the *nnp*-IBJT is feasible for controlling transport of both inorganic anions as well as smaller negatively charged biomolecules.

Figure 5. Actively modulated Glu transport. The emitter electrolyte comprises 0.05 M Glu and 0.05 M NaCl while the collector electrolyte contains a enzymatic detection kit for Glu. In the cutoff mode no color change is observed 40 μm from the outlet. When switched on the Glu induced color change increases until the device is turned off. Upon delivery stoppage the Glu and dye concentration at the outlet starts to decrease due to diffusion.

With this work, we have demonstrated how *npn*-IBJT's can be constructed utilizing standard microfabrication techniques. Currently, the transistor characteristics of our *npn*-IBJT's including high on-off ratios, stable current levels and dynamic modulation outperform other kinds of ionic transistors running at physiological conditions. The design is prepared for integration of both *npn*- and *pnp*-IBJT's manufactured on the same chip without additional fabrication steps. As the *n*- and *p*-channels are vertically separated from each other they can cross without the need of additional insulation and vertical interconnects. Further, the improved design allows for uncrosslinked polymer electrolytes to be used as the junction, offering greater choices with respect to materials in general and opens up for future performance improvements. All together, our findings lay the groundwork for realization of complementary ionic circuits, *e.g.* addressable delivery systems for charged biomolecules. We envisage that such ionic circuits will have impact in various fields including sensors²⁵, lab-on-a-chip²⁶, drug delivery²⁷ and electrochemical components²⁸.

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Supporting Information Available : Materials and methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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