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Ion diode logics for pH control

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Electronic control over the generation, transport, and delivery of ions is useful in order to regulate reactions, functions, and processes in various chemical and biological systems. Different kinds of ion diodes and transistors that exhibit non-linear current versus voltage characteristics have been explored to generate chemical gradients and signals. Bipolar membranes (BM)s exhibit both ion current rectification and water splitting and are thus suitable as ion diodes for the regulation of pH. To date, fast switching ion diodes have been difficult to realize due to accumulation of ions inside the device structure at forward bias – charges that take a long time to deplete at reverse bias. Water splitting occurs at elevated reverse voltage bias and is a feature that renders high ion current rectification impossible. This makes integration of ion diodes in circuits difficult. Here, we report three different designs of micro-fabricated ion bipolar membrane diodes (IBMDs). The first two designs consist of single BM configurations, and are capable of either splitting water or providing high current rectification. In the third design, water-splitting BMs and a highly-rectifying BM are connected in series, thus suppressing accumulation of ions. The resulting IBMD shows less hysteresis, faster off-switching, and also a high ion current rectification ratio as compared to the single BM devices. Further, the IBMD was integrated in a diode-based AND gate, which is capable of controlling delivery of a hydroxide ions into a receiving reservoir.

Introduction

In recent years, the use of organic electronics to regulate functions of biological systems has received increasing attention^{1–3}. Transistors^{4,5}, electrodes^{6–8}, and diodes⁹ have successfully been explored to selectively sense and regulate a vast array of processes of eukaryotic cell systems. Organic electronic materials possess several unique features which make them of particular value in biological applications: flexibility¹⁰, softness¹¹, stability in physiological conditions¹², electronic and ionic conduction¹³, and biocompatibility¹⁴. These properties promise for future organic bioelectronics platforms that enable radically new therapy, diagnostics, and monitoring methods. In one particular application, the combination of a polyelectrolyte and a conjugated polymer has been explored for controlled electrophoretic transport of ions and charged biomolecules to regulate signaling and formation of cell cultures^{13,15}, tissues¹⁶ and peptide aggregates¹⁷. This so-called organic electronic ion pump (OEIP) offers electronic addressing and precise control over the delivery of biomolecules at high spatiotemporal resolution. Further, delivery of substances is achieved at zero fluidic convection and advection, and no moving parts are needed in order to operate the OEIP. However, the electronic current versus voltage characteristics of the OEIP equals that of an ordinary resistor, and in order to achieve more complex circuits for ion delivery, non-linear device characteristics are needed – such as the ones provided by transistors and diodes. Several types of transistors that can gate and amplify ionic currents have been described in the literature^{18–22}. Diodes are attractive due to their rectification property and they can be used in simple logic gate circuits and also as the addressing element in cross-point matrix systems. Several different types of ion diodes have previously been reported, based on either nanofluidic channels^{23–25},

hydrogels^{26–29}, or BMs^{30–32}. Nanofluidic diodes exhibit ion current rectification due to surface charges along nanometer-sized channels, which offer selective ion transport. The nanofluidic diodes typically fail to operate properly at high electrolyte concentration, as the Debye screening length is decreased^{19, 23–25}. Thus, they are not suitable for use in applications that require operation at high salt concentration, e.g. operation at physiological conditions. Electrolytic diodes consist of a hydrogel which separates an acidic and an alkali solution^{26, 27}. In forward bias the conjugated base and acid migrates through the hydrogel, while in reverse bias the conductivity is reduced due to H⁺ and OH[–] recombination. Although potent as a diode, the acidic/alkali electrolytes impose limitations for possible applications.

BMs are composed of cation- and anion-selective membranes stacked together, and their ion current rectification properties have been well studied in the past^{30, 33, 34}. Cation- and anion-selective membranes contain negative or positive fixed ionic charges, respectively, typically covalently bound to a polymer backbone. The fixed charges are compensated by mobile ions of opposite charge (counterions), while ions of the same charge (coions) are repelled (Donnan exclusion). Therefore the membrane favors transport of counterions, as long as the surrounding electrolyte concentration remains below the fixed charge concentration of the membrane. Cation and anion selective membranes can therefore be regarded as the ionic equivalent to *p*- and *n*-type semiconductors, and a BM is thus expected to behave similarly to a *pn*-junction diode. A BM is in forward bias when the anode is connected to the cation selective side of the BM (Fig. 1A). In forward bias, the counterions on both sides of the BM can migrate in the electric field towards the BM junction. This results in an accumulation of mobile ions

along the interface of the two membranes, giving rise to a high ionic concentration and thus a high conductivity. The high ion concentrations within the BM junction can cause Donnan exclusion to fail, leading to coions migrating into the ion selective membranes³⁵.

In reverse bias, the counterions migrate away from the BM junction. As Donnan exclusion prevents coions from migrating through the cation and anion selective membranes to the BM junction, the junction is depleted of mobile ions. Due to the drop in ion concentration, the conductivity through the BM decreases. Thus, the current in forward bias is significantly larger than the current in reverse bias, *i.e.*, ion current rectification is obtained.

After depleting the BM junction in reverse bias, the electric potential mainly drops across the junction. Under certain circumstances, such as a close proximity between the membranes and sufficiently high applied voltage, the electric field between the membranes can accelerate the dissociation of water, *i.e.*, water is split into H⁺ and OH⁻^{34, 36}. This causes a significant current in reverse bias, and the rectification of the BM diminishes. Such water splitting typically limits the operational voltage range for current rectification to ± 1 V. Furthermore, BMs may suffer from hysteresis, as the ions that accumulate inside the BM during forward bias need to be extracted during reverse bias operation before ion depletion occurs and a stable low reverse current is obtained. Previously reported micro-fabricated IBMDs experiences such hysteresis^{35, 37}, and the potential loss of current rectification due to water splitting needs to be addressed.

In this paper, we report on the combination of different BM configurations to mitigate the ion accumulation hysteresis. The reported ion diode operates at physiological conditions without significant hysteresis at voltages above 1 V. Thus, fast switching at high ion concentrations is achieved. The resulting IBMD provides ion current rectification combined with water splitting behavior, which allows for realization of IBMD water splitting circuits. Finally, we present an AND water-splitter logic gate built up of such IBMDs.

Experimental

Anion selective membrane solution

The process for obtaining the anion exchange material (q-PVBC) has been described previously³⁷. Briefly, poly(vinylbenzyl chloride) (Sigma-Aldrich) was dissolved in tetrahydrofuran (200 mg/ml), and 500 μ l of the solution was mixed with 76 μ l dimethylbenzylamine (>98%, Alfa Aesar). The mixture was heated in a water bath at 50 °C for 1 h, after which excess solvents were removed and the precipitate was washed in acetone. The precipitate was then dissolved in 1 ml deionized water and mixed with 1 ml 1-propanol and 6.6 μ l of a 5M diazabicyclo[2.2.2]octane (Sigma-Aldrich) solution in ethanol.

Device fabrication

The fabrication of BMs followed a previously reported process with some modification³⁷. Sheets of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on polyethylene terephthalate (PET) (AGFA-Gevaert OrgaconTM F-350) were cleaned with acetone and water and baked (5 min, 110 °C). Poly(methyl methacrylate) (PMMA, Sigma-Aldrich, average m.w. ~120000, 4 mg/ml in Diethyl carbonate) was spin

coated on top (4000 rpm for 30 s, 5 min 110 °C bake) followed by a layer of Shipley S1805G2 (4000 rpm for 30 s, 5 min 110 °C bake). The photoresist was exposed using a Karl Suss MA/MB 6 mask aligner and developed in Microposit MIF319 developer to pattern the electrodes and cation selective channels. After a bake (5 min, 110 °C) the pattern was dry-etched in a CF₄/O₂ plasma for 25 s, and the remaining photoresist was removed using acetone and rinsed in isopropanol. A Microposit S1813G2 photoresist layer (4000 rpm, 10 min 110 °C bake) was subsequently patterned to expose the cation selective channels. The channels were overoxidized by incubation in aqueous sodium hypochlorite solution (1% (vol/vol)) for 60 s, followed by photoresist removal using Shipley 1112A Remover and incubation in aqueous sodium chloride (0.1 M, 2 min). After a 15 min 110 °C bake, a 2.5 μ m thick SU8-layer (SU8-2002, MicroChem) was spin coated on top (1000 rpm for 30 s) and patterned according to the manufacturer's instructions to define the active areas of the BMs. The electrodes and cation selective channels were protected by patterning a Shipley S1813G2 layer on top, which was hard-baked for 1 h at 110 °C. The anion selective membrane was deposited by spin coating (1500 rpm for 30 s) and baked for 1 h at 110 °C. The anion selective membrane was protected during further processing steps by spin coating PMMA (40 mg/ml in DEC, 2000 rpm for 30 s, 10 min bake 110 °C) followed by patterning of anion selective channels with a Shipley S1813G2 (4000 rpm, 30 s, 10 min 110 °C bake) photoresist layer. The exposed anion selective material was etched with a CF₄/O₂ plasma (100 s) and the remaining photoresist was removed with acetone and rinsed in isopropanol. A final layer of 10 μ m thick SU8 (SU8-2010, MicroChem) was spin coated (3000 rpm, 30 s) and patterned to seal the BMs with direct contact membranes, or to define the junction for the BMs with neutral electrolyte. The neutral electrolyte (poly(ethylene glycol) (PEG), m.w. 950-1050, Sigma) was dissolved in cyclopentanone (500 mg/ml) and printed into the openings of the SU8 using an inkjet printer (Fujifilm Dimatix Material Printer 2800). The neutral electrolyte was sealed using polydimethylsiloxane (PDMS, Sylgard 184, 10:1 curing agent ratio, cured 1 h at 100°C) and silver contacts were painted on the electrodes and baked for 10 min (100 °C).

Device architectures

BMs were fabricated between PEDOT:PSS electrodes (Fig. 1B) by sandwiching overoxidized PEDOT:PSS with q-PVBC. Overoxidation of the PEDOT:PSS terminates the electronic conductivity of PEDOT while the cationic conductivity of PSS is retained³⁸, converting the material to a cation selective membrane. The PEDOT:PSS electrodes, covered with aqueous electrolytes, transduce electronic and ionic currents via the electrochemical reaction $\text{PEDOT}^+:\text{PSS}^- + \text{M}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{PEDOT}^0 + \text{M}^+:\text{PSS}^-$. Two configurations of the BM junction were used. In the first, the anion selective channel overlaps the cation selective channel by 100 μ m through an opening in the SU-8 B layer (Fig. 1C), resulting in a BM with a direct-contact junction (IBMD1). In the second configuration, the anion selective channel is separated from the cation selective channel by a 100 μ m long PEG electrolyte (Fig. 1D). This resulted in a BM configuration with a neutral electrolyte junction (IBMD2). By combining BMs with both IBMD1 and IBMD2 configuration,

Fig. 1. Illustrations of the junctions of biased BMs, and the IBMD designs used in this work. (A) Ion movement in a BM at forward and reverse bias.

The mobile ions migrate in the electric field (E), resulting in ion accumulation (forward bias), ion depletion (reverse bias), or water splitting in the BM. The current through the BM is high during forward bias and water splitting, and low during reverse bias. (B) Illustration of a micro-fabricated IBMD device. The BM is connected to two PEDOT:PSS electrodes via aqueous electrolytes. (C) Schematic illustration of a direct contact junction BM (IBMD1), (D) a neutral electrolyte junction BM (IBMD2), and (E) combined BMs (IBMD3). IBMD3 is composed of two IBMD1s and one IBMD2.

a third device is obtained (IBMD3, Fig. 1E). To optimize the performance of the IMBD3 device, a wider channel width was used for IMBD1 (200 μm) compared to IMBD2 (50 μm). The total lengths of the BMs, with channels, were 1.4 mm.

Device characterization

Prior to characterization the devices were incubated in deionized water overnight. Aqueous sodium chloride solution (0.1 M) was used as electrolytes. Before testing, the devices were switched between reverse and forward bias at least 10 times to archive stable performance. Switching and current-voltage measurements were performed at 4 Hz with a Keithley 2602A source meter programmed via LabVIEW. Current-voltage characteristics were obtained with a scan rate of 20 mV/s. Image time lapses were recorded using a Nikon SMZ1500 microscope with a Nikon DS-Fi1 color camera and LED illumination. To visualize pH changes a universal pH indicator (Sigma-Aldrich) was added to the electrolyte.

Results and discussion

BM with direct contact junction (IBMD1)

We first characterized IBMD1 (Fig. 1C) by monitoring the current through the device while scanning the voltage from negative (reverse bias) to positive (forward bias) (Fig. 2). Different regimes in the current-voltage plot can be distinguished. At positive voltages the current is approximately linearly dependent on the applied voltage and is relatively high. For low negative voltages, (-2 V to 0 V), the resistance is also linearly dependent versus the voltage but the conductivity is significantly lower. At larger negative bias, the conductivity increases with the voltage. The three regimes correspond to forward and reverse bias and water splitting operation of the BM, respectively. During

Fig. 2. Current-voltage characteristics for an IBMD1 device. The voltage is scanned from negative to positive bias, as indicated by the arrow. The BM is highly conducting in forward bias and significantly less conducting at reverse bias between 0 to -2 V. The linear current versus voltage slope in forward bias originates from the resistance of the two channels. Below -2 V water splitting occurs resulting in high conductivity. The produced H⁺ and OH⁻ during water splitting can be detected in the anode and cathode electrolytes, respectively, using pH indicators (insert image, anode is on the left side, scale bar is 500 μm. The red and blue color correspond to pH<4 and pH>10, respectively).

water splitting, the generated ions are transported away from the junction and replaces the previous ions of the selective channels, resulting in H⁺ and OH⁻ being released at the anode and cathode, respectively (see insert in Fig. 2). For the IBMD1 presented in Fig. 2, the current rectification ratio is about 50 at ±1.5 V, while at ±4 V it drops down to 3. It is thus clear that BMs with direct contact membranes are only suitable as diodes, *i.e.*, as current rectifiers, in a limited voltage range where water splitting is avoided. Thus, this configuration cannot be used in applications where current rectification needs to be combined with water splitting, such as in diode circuits for pH control.

BM with neutral electrolyte junction (IBMD2)

To avoid the water splitting in BMs one can introduce a neutral electrolyte gap between the two membranes^{34, 39-42}. Recently, this strategy was employed in ion bipolar junction transistors (IBJTs)²². The IBJT is a three terminal iontronic device that enables base-addressed amplification of ionic currents. When this IBJT is connected in a diode configuration an ion current rectification ratio of about 40 is reached²². For a BM diode, only two channels into the junction are necessary, and the dimensions of the neutral electrolyte can thus be reduced (IBMD2, Fig. 1D). The current-voltage plot for the IBMD2 device is shown in Fig. 3A. Here, only two regimes are found. At positive voltages (forward bias) the resistance is linearly dependent on the applied voltage and the conductivity is relatively high. For negative voltages, the resistance remains linear but the conductivity is relatively lower and the current remains low (< 1 nA) even for elevated negative voltages (< -1.5 V). The reverse current density at -4 V in IBMD2 is less than 0.5% of that in IMBD1. A neutral layer inside a BM has been proposed to distribute the potential drop over the interfaces and the neutral layer, thereby reducing the electric field at the interfaces^{39,41}. The lower electric field results in a decrease in the electric field enhanced water dissociation rate³⁴. The observed reverse current could be due to coion migration in the ion selective channels, autodissociation of

water in the PEG gel, or a small amount of electric field enhanced water dissociation. As a consequence, the current rectification ratio remains high even at voltages beyond ± 1 V, and a rectification ratio exceeding 200 at ± 4 V is observed in the IBMD2 device.

Even though the IBMD2 structure can exhibit good static performance, *i.e.*, high ion current rectification, the device suffers from hysteresis due to ion accumulation when swiftly scanned from forward to reverse bias (see reverse scan in Fig. 3A). Fig. 3B gives the switching behavior of an IBMD2 upon switching between ± 3 V, together with the integrated current through the device (*i.e.*, the amount of charge injected into or extracted from the BM). When switching from reverse to forward bias the current initially increases exponentially, followed by a linear regime. The constant rise in current is due to a continuous accumulation of ions at the junction of the BM, which increases the conductivity. Due to the lack of stable on-current even after 120 s of forward bias operation, the on-current was approximated with the current obtained 30 s after the switch. The rise time for the current to increase from 30% to 70% of this value ($t_{\text{on}}^{\text{IBMD2}}$) is approximately 0.5 s. As the BM is switched from forward to reverse bias, three regimes (annotated with 1-3 in Fig. 3B) are observed. During the first regime the current remains high. At this stage, the ion concentration inside the BM is still high, and thus the reverse bias current is also high. In the second regime there is an abrupt decrease in the current. At this point, nearly all the injected charges are extracted, which results in a decrease in conductivity. Finally, the current approaches a low steady-state reverse bias current. The turn-off time ($t_{\text{off}}^{\text{IBMD2}}$), defined as when the current drops below 30% of the forward current, is 108 s. Evidently, the switching time from forward to reverse mode is to a large extent dependent on the amount of time the device has been biased in the forward direction (*i.e.*, the amount of charges accumulated within the neutral region). The associated large hysteresis when switching the IBMD2 makes it difficult to utilize it as a diode (rectifier) in ionic circuits.

Low hysteresis ion BM diode (IBMD3)

The performance of the IBMD2 structure would be significantly improved if accumulation of ions during forward bias operation could be suppressed. This could be achieved if HCl and NaOH were used as anode and cathode electrolyte, respectively. The counterions in the BM would then be represented by H^+ and OH^- , which would continuously recombine into water at the junction. The fact that IBMD1 exhibits water splitting during reverse bias inspired us to utilize the H^+ and OH^- produced *in situ* from such BMs for injection into the neutral electrolyte of a third BM (Fig. 4A). Two IBMD1s and one IBMD2 configurations were connected cathode-to-cathode and anode-to-anode, *i.e.*, the outer water splitting IBMD1s were connected in reverse orientation with respect to the central IBMD2 configuration (Fig. 1E). The current-voltage characteristics of the resulting IBMD3 device are given in Fig. 4B. The current-voltage curve exhibits three characteristic features. At negative voltages the current is very low. In this region the central IBMD2 structure is in reverse bias, while the two IBMD1 structures are forward biased. Thus, the main voltage drop in the device occurs across the IBMD2, resulting in a low ion current (reverse bias mode). In forward bias, for voltages less than 2 V, the current remains low, but a

Fig. 3. Diode characteristics for an IBMD2 device with neutral electrolyte junction. (A) Current-voltage characteristics for an IBMD2 device when scanning from -4 to 4 V (forward scan) and from -4 to +2 and back to -4 V (reverse scan). The arrows indicate scan direction. The forward scan shows clear diode characteristics with reverse and forward regimes. In the reverse scan from +2 to -4 V, hysteresis appears at reverse bias due to ion accumulation in the BM. Note that the lower conductivity in forward bias compared to the IBMD1 device in Fig. 2 is due to thinner channels in the device, leading to higher resistance. (B) Switching performance at ± 3 V of an IBMD2 device. The rise time ($t_{\text{on}}^{\text{IBMD2}}$) during the on-switch is fast (approximately 0.5 s, see insert), while the off-switch ($t_{\text{off}}^{\text{IBMD2}}$) is relatively slow (108 s). Almost all injected charge during forward bias needs to be extracted after the switch to reverse bias before a stable and low reverse current is obtained.

small peak arises in both scan directions. In this voltage range, the applied voltage is not enough to cause any pronounced water splitting at the two IBMD1s, and the two BMs are still in the low conducting reverse bias mode. The two peaks observed in the forward and reverse scans are due to extraction of small amounts of accumulated ions in the individual BMs, during switching from their respective forward to reverse bias. Above 2 V the current starts to increase non-linearly versus the applied voltage, followed by a linear increase versus voltage above 7 V. The change in conductivity arises from the applied bias exceeds the threshold for water splitting at the two IBMD1 junctions. Thus, both IBMD1s are in the water splitting mode while the central IBMD2 is in the forward bias mode, resulting in forward bias operation for the series of BMs. During the reverse scan, only a

small amount of hysteresis is observed. Since most of the ions injected into the neutral electrolyte of the IBMD2 structure during forward bias are H^+ or OH^- , which can recombine to form water, the ion accumulation in the neutral region of the IBMD2 central structure is reduced compared to the single IBMD2 device.

To study the transient behavior of the IBMD3, the device was biased by swiftly switching the polarity between the reverse and forward mode ($\pm 8\text{ V}$, Fig. 4C). A higher voltage, compared to the IBMD2, was used to compensate for the potential drop introduced by the water splitting IBMD1s. When switching from reverse to forward bias, the current increases roughly linearly, followed by a stabilization of the current. The rise time ($t_{\text{on}}^{\text{IBMD3}}$) is 4.2 s. The on-current of the IBMD3 is stable, as opposed to the constantly increasing current for the IBMD2 (Fig. 3B), which indicates that the ion concentration inside the neutral electrolyte is not constantly increasing over an extended time. Upon switching the IBMD3 from the forward to reverse bias mode, a short but significant current peak is observed (4 s, located at around 135 s, see Fig. 4C), before the current returns to a stable low level. Initially after reversing the bias mode, there are some residual salt ions and non-recombined H^+ and OH^- ions left in the junction and the extraction of these ions is likely the cause of the current peak. However, the amount of extracted charge, integrated from the reverse bias current, is only 4% of the integrated current during the forward bias mode. Comparing these results with the equivalent results from the IBMD2, we find that the time it takes to switch the device from forward to reverse current mode has decreased considerably. The IBMD3 is able to reach a reverse current $<30\%$ of the forward bias current after only 4.3 s ($t_{\text{off}}^{\text{IBMD3}}$), a significant improvement compared to the IBMD2 turn-off time of 108 s. The measured current rectification ratio for the IBMD3 at $\pm 8\text{ V}$ was over 300.

Ion diode-based AND gate

The realization of low hysteresis ion diodes (IBMD3) inspired us to design and test diode logic circuits. In addition to a faster off-switching speed, the IBMD3 allows for the translation of an electric current to a chemical output, in this case, the delivery of H^+ and OH^- ions. A three diode configuration (shown in Fig. 5A and Fig. 5B) was used to realize an AND ion current gate for OH^- delivery. A three-diode circuit was used, instead of a traditional two-diode AND circuit, since this more complicated circuit minimizes cross-talk between devices connected through the same electrolyte. Furthermore, the three-diode circuit allows for addressing connections to be located on separate layers. Both of these features typically simplify integration with other ionic devices^{22, 37}. Fig. 5C illustrates the expected currents through the devices for four input voltage combinations applied to the two electrodes. In the first combination (i) both electrodes are positively biased. Thus the output diode will be reverse biased, and a current can only run between the two input electrodes if $V_1 - V_2$ is greater than the threshold of the two input diodes. If V_1 is switched to negative voltage (ii) all diodes will remain in the reverse bias mode. If V_1 is kept positive and V_2 is switched to negative voltage (iii) both the input 1 and the output diode are in forward bias. However, if V_1 is high enough the voltage at the junction of the diodes will be positive and the output diode will remain in reverse bias. This results in a large current between the

Fig. 4. Diode characteristics for a combined IBMD3 device. (A) Ion movement during forward and reverse bias of the IBMD3 device. At reverse bias, the neutral electrolyte of the IBMD2 is ion depleted. Under forward bias water is split in the two IBMD1s, and the produced H^+ and OH^- are transported to the neutral electrolyte of the IBMD2, where recombination to water can occur. (B) Current-voltage characteristics for IBMD3 device. The scan starts and ends at -8 V , and the scan direction is indicated by the arrows. At negative voltages the current is low, while for positive voltages higher than 2 V the current increases. The hysteresis during the reverse scan from $+8\text{ V}$ to -8 V is notably smaller than for the IBMD2 device (see Fig. 3A). (C) Switching performance at $\pm 8\text{ V}$ of an IBMD3 device. After the switch to $+8\text{ V}$ the current increases to a stable forward current, with a rise time $t_{\text{on}}^{\text{IBMD3}}$ of 4.2 s. At the switch to -8 V , there is a sharp peak in the current, followed by a quick return to the stable reverse bias current. The current falls to below 30% of the forward bias current ($t_{\text{off}}^{\text{IBMD3}}$) in 4.3 s. The amount of charge injected into the device during the forward bias mode is significantly larger than the extracted amount during the switch to the reverse bias mode.

two input electrodes and no current through the output terminal. In the last voltage combination, both inputs are switched to negative voltage (iv). Here, the output diode will be in forward bias, resulting in a current through the output electrode (on-mode).

In Fig. 5D the voltage of the input electrodes are switched between the four combinations of voltages ($V_1 = 6$ or -3 V , $V_2 = 4$ or -12 V), and the current through the outlet electrode is recorded. Fig. 5E shows the simultaneous recording of color change of pH

Fig. 5. Description and function of the ion diode AND gate circuit for OH^- delivery. (A) Schematic drawing and (B) illustration of the AND circuit, showing the two input diodes and the output diode. Each diode is composed of one IBMD2 connected to one IBMD1 towards the electrode and one common IBMD1 in the middle of the circuit. (C) The current through the circuit and the bias of the individual diodes for the four combinations of input voltages. Red color indicates reverse bias, and green color indicates forward bias. Only the type iv combination results in a current through the output diode. For simplicity, the resistors in the circuit are not shown. (D) Measured current through the output diode and pH change recorded at the outlet of the output diode as the voltages applied to the input electrodes are varied. A stable current is only obtained when both inputs are low, resulting in a delivery of OH^- which is detected as a change in color corresponding to alkali pH. (E) Snapshots of the outlet of the output diode. After both inputs have been set to low voltage (i.e., the on-state), a blue color change corresponding to alkali pH is observed at the outlet. The color change disappears once the circuit is switched back to off-state, indicating diffusion of the delivered OH^- . The scale bar is 200 μm .

indicator at the outlet (due to delivery of OH^-). The applied voltages were chosen to minimize the current in the off-modes and to maximize the current in the on-mode. The device is first switched between the three off-modes, which only result in transient current peaks and no recorded color change at the output electrode. Upon application of $V_1 = -3 \text{ V}$ and $V_2 = -12 \text{ V}$, a steady-state current runs through the output electrode and an associated color change (corresponding to alkali pH) is observed.

As the device is switched back to off-mode, the current goes back to zero, and the color change disappears as the delivered OH^- diffuse away (Fig. 5E). A complementary design, where the diodes are reversed as compared to the design in Fig. 5 and which delivers a current of H^+ during the on-mode, is presented in supplementary Fig. S1.

Conclusions

Although the current rectification properties of bipolar membranes are already well known, their use for realizing ion diodes has been scarce. Previous work on using BM structures as ion diodes has shown either problems with water splitting in reverse bias or hysteresis due to ion accumulation during forward bias. In this work we have presented a solution for minimizing the hysteresis in ion BM diodes without restricting the choice of electrolyte. In the presented ion diode, H^+ and OH^- formed during water splitting are injected into the BM, where they recombine to water, thus avoiding ion accumulation. This results in fast switching from on- to off-state, as only a small amount of charge needs to be extracted. Additionally, as H^+ and OH^- are created during forward bias operation, the presented ion BM diode can be used as a pH actuator. The rectification and pH changing properties of our ion diode enabled us to use it as an electric-to-ionic AND gate. In future work such a device could be effective in creating electronically addressed controlled pH gradients, which could be useful for regulation of pH dependent processes, such as bone formation⁴³, tumor cell growth⁴⁴, neuron signaling function⁴⁵ or peptide aggregation⁴⁶. Specifically, such a device could replace the simple resistive OEIP previously used for spatiotemporal control of peptide aggregation¹⁷, with the advantage of addressability and H^+/OH^- delivery without requiring acidic/alkali source electrolyte. Furthermore, we expect our low-hysteresis fast-switching ion diode to be useful in combination with other ionic devices, such as ion bipolar junction transistors, for creating more complex ionic circuits.

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Fig. S1. Description and function of the complementary ion diode AND gate circuit. (A) Schematic drawing of the complementary AND circuit. To archive the complementary circuit, the diodes are reversed compared to the circuit in Fig. 5. (B) Measured output current and induced pH change as the voltages applied to the input electrodes are switched. Only when both inputs are high is a stable current is obtained, giving the on-state of the circuit. During the on-state H^+ is released at the outlet of the output diode (instead of OH^- as in Fig. 5), which is detected as an acidic color change. (C) Snapshots of the outlet of the output diode. When the circuit is in the on-state, a red color change, corresponding to acidic pH, is observed at the outlet. As the circuit is switch back to the off-state the color change is reverted, indicating diffusion of the delivered H^+ . The scale bar is 200 μm .