

Supplementary Information

High-flux ionic diodes, ionic transistors and ionic amplifiers based on external ion concentration polarization by an ion exchange membrane: a new scalable ionic circuit platform

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1. The chip fabrication process.

The fabrication process of the microfluidic-anion exchange membrane hybrid chip was adopted from reference 25. The anion exchange membrane (AEM) was a commercially-available heterogenous anion exchange membrane obtained from Mega a.s., Czech Republic (<http://www.mega.cz/heterogenous-ion-exchange-membranes-ralex.html>). The AEM consists of fine polystyrene-divinylbenzene particles with strong basic quaternary ammonium groups ($R-(CH_3)_3N^+$) supported by polyethylene as a binder and polyamide / polyester textile fiber. The membrane has a thickness around 450 μm when dry and around 700 μm after it is swelled in water with a pore size of around 1 nm and an exchange capacity of 1.8 mval/g.¹⁵ A 1.1 mm \times 1.6 mm AEM was cut and embedded into a two-component fast curing polyurethane resin (TAP Plastics, 1:1 Side A: Side B, cured at room temperature for 30 min). The resin pellet was molded by a silicone mold (TAP Plastics, 10:1 Silicone:Catalyst, cured at room temperature for 24 hrs) which was casted from a primary mold created on a poly(methyl methacrylate) (PMMA) sheet using a micro-milling machine (Roland IM-01 iModela). It had a through hole from top to bottom where the AEM was exposed. A PMMA tube was then glued to the resin pellet as the “G” terminal reservoir with UV curable glues (Loctite 3492 and Acrifix 192). The main body of the chip with a “T” shape microfluidic channel consisted of three layers of polycarbonate sheets. The microfluidic channel was structured by cutting the middle polycarbonate sheet on a plotter (Graphtec 7000). The openings of the channel were cut on the top polycarbonate sheet. The three structured polycarbonate sheets were then

aligned and thermally bonded together (170 °C for 40 min). Cut pipet tips with a filter paper on the bottom as buffer reservoirs for electrical connection and Tygon tubings as fluidic inlets and outlets were fixed by UV curable glues into their designated places on the top polycarbonate sheet. A layer of 1% agarose gel was placed in the bottom of each cut pipet tip reservoirs to prevent possible bubble entry during electrical measurements. The resin pellet with the AEM was finally glued to the top polycarbonate sheet with UV curable glues on top of the intersection region of the “T” channel, through a 2 mm × 1.5 mm opening. The device was then infused and soaked with 0.1 X Phosphate Buffer Saline solution (PBS, diluted from 10 X PBS solution, Fisher Scientific) for 24 hrs to swell the AEM prior to use.

2. Electrical characterization.

A 0.1 X PBS solution dissolved with 100 μM Rhodamine 6G (Sigma) for fluorescence imaging was used as the electrolyte solution in all electrical characterization experiments. All electrical measurement data was obtained by a Keithley 2636A Dual-Channel System SourceMeter Instrument while the fluorescence images were captured by a web camera (Logitech, HD Pro webcam, C920) in real-time. The Keithley 2636A and the web camera were synchronized and controlled by MATLAB. In all electrical characterizations, the potential at the “G” terminal V_G and the “B” terminal V_B were turned on 300 s before applying the potential at the “D” terminal and the “S” terminal, to ensure a desired ion concentration at the intersection region for each device operation before the measurement. In all electrical measurement experiments requiring a V_D sweep, I_{output} at each V_D value was measured for 80 s before sweeping to another V_D value (data shown in Fig. 2b, 2c, 3c, 4b). In the ionic transistor power amplification experiment shown in Fig. 4d and 4e, P_{input} and P_{output} at each V_G were measured for 800 s. The average P_{input} and P_{output} were then calculated for the 800 s time interval.

3. Stability of the ionic transistor as an ion current switch.

Figure S1 shows the stability of the ionic transistor when it is used to switch off the output current through the “D-S” output fluidic channel. The I_{output} is measured for 10 minutes without applying a V_G or with a $V_G = 20$ V, respectively. Both the intrinsic “ON” state output current (~ 40 μA without applying V_G) and the “OFF” state output current (~ 0.27 μA , with a $V_G = 20$ V) stay stably during the entire measurement.

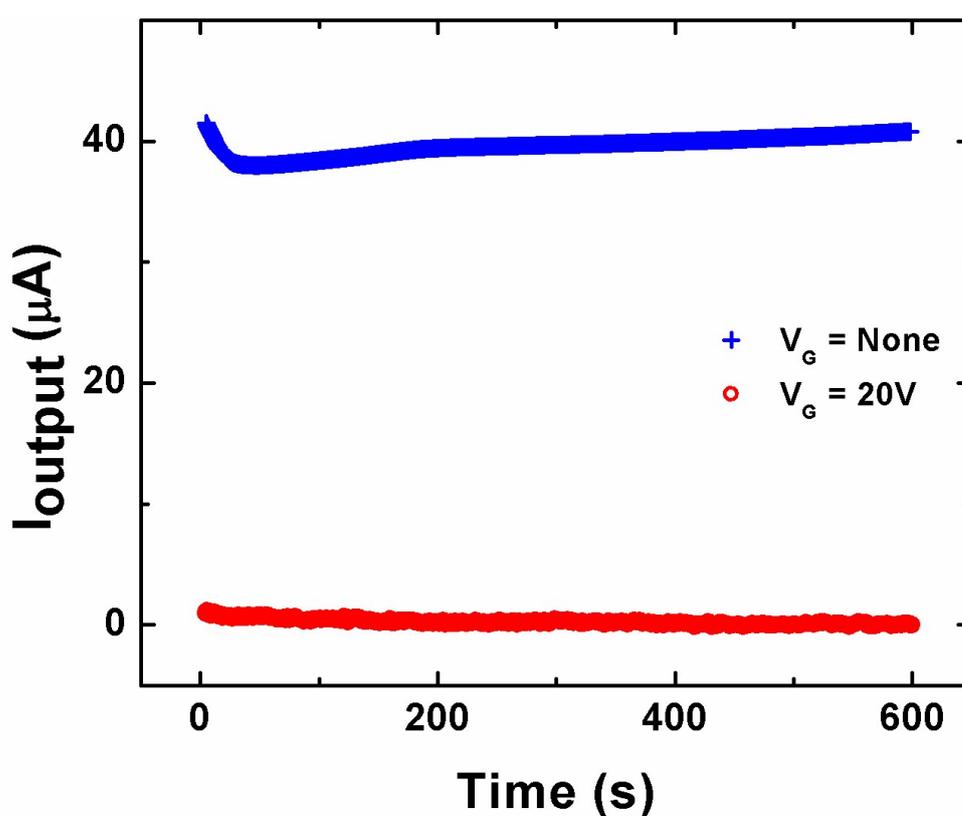


Figure S1. The stability of the output current for the ionic transistor in both the “ON” state and the “OFF” state. The output voltage V_D is 10 V for both measurements.

4. Inversion of Electric field direction across the AEM between the linear region and the amplification region of the ionic transistor.

Figure S2 shows the input current I_{input} across the AEM from the “G” terminal to the intersection region during the experiment when V_G is -5 V and V_D sweeps from -5 V to -25 V

with 0.5 V as a step size. When $|V_D|$ is small, the ionic transistor is in the linear region with $V_{junction}$ higher than V_G , so that I_{input} is negative. As $|V_D|$ increases, $V_{junction}$ becomes lower than V_G , causing the electric field direction across the AEM reverses which is indicated by the change of the sign of I_{input} . When $|V_D|$ is sufficiently high, the depletion zone is formed so that I_{input} is stabilized. It indicates that the ionic transistor is in the amplification region.

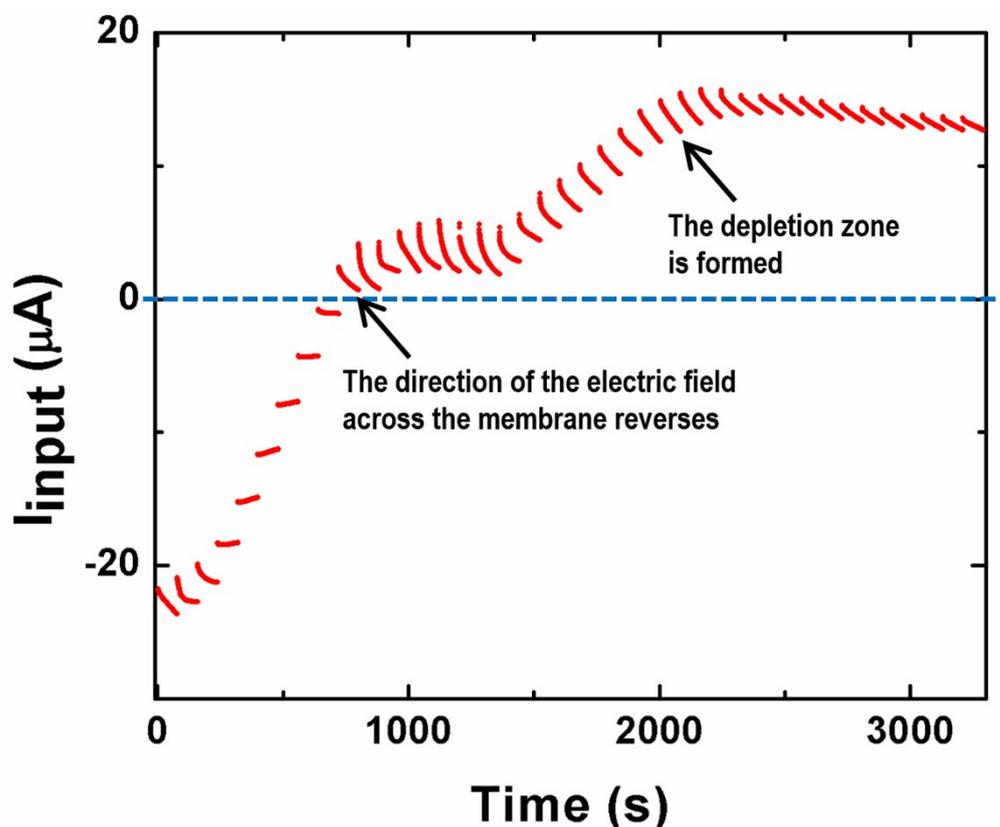


Figure S2. The sign change of I_{input} (defined as the ion current from the “G” terminal to the intersection region across the AEM) indicates the electric field direction inversion across the AEM as the ionic transistor works in the linear region or the amplification region.

5. Real-time fluorescence video for verifying the ion current amplification mechanism.

The attached Video S1 consists of a series of real-time fluorescence images showing the ion current amplification mechanism. In this experiment, V_G is -2.5 V and V_D is -20 V. Eight frames from this video are chosen in Fig. 4c. After 600 s of the start of the experiment, the ion depletion zone can be observed from the intersection region to the “D” terminal. The video

shows that due to the relative relationship between ϕ_{gnd} (potential at the “S” terminal), V_{junction} and V_D , positively charged fluorescence molecules are transported from the “S” terminal to the intersection region, and then across the depletion zone to the “D” terminal to achieve the output ion current amplification.