Ionic Circuits

DOI: 10.1002/anie.200900045

Ionic Circuits Based on Polyelectrolyte Diodes on a Microchip**

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A polyelectrolyte diode is a device based on strong Donnan exclusion in the electrostatic junction between two oppositely charged polyelectrolytes.[1] This junction system acts as a rectifier similar to a silicon-based electronic p–n junction.[2] The counterions in each polyelectrolyte plug carry charge in a manner similar to holes and electrons in a solid-state diode. A forward bias makes the counterions migrate toward the junction, while a reverse bias drives them from the polyelectrolyte phases to bulk solutions (see the Supporting Information). Owing to a difference between the resistances under forward and reverse bias across the junction, this electrical circuit exhibits nonlinear characteristics.

Since rectification in a polyelectrolyte system was first proposed by Bockris and co-workers in 1959,[3] a few reports have been published concerning their nonlinear behavior,[4–6] theoretical modeling,[7,8] experiment results,[9] and water dissociation.[10] Such systems have increasingly attracted attention, as Shashoua suggested the possibility of using a polyelectrolyte junction as a model for a biological system by mimicking the potential spike of a neuronal membrane.[11] They may lead to interesting applications such as analogues of nonlinear electronic systems and model systems for the asymmetric functions of cell membranes.

However, polyelectrolyte systems have witnessed only minor advances in terms of both fundamental understanding and useful applications since the Bockris model was proposed. In the reported systems, the current versus voltage behavior (*I*–*V* curve) was not governed by the impedance at the polyelectrolyte junctions but was significantly affected by the electrochemical reactions at the electrode surfaces. This dependence arises because the resistance between the electrodes and the solutions was not negligible compared with that at the polyelectrolyte junction (see the Supporting Information). More importantly, no miniaturized network system has been reported to date. Such miniaturization is essential not only for quick response to an external electric input but also for logical integration of many polyelectrolyte junctions on a chip for more complex circuits and intelligent devices.

Another obstacle preventing progress in ionic circuits based on polymer junctions is a lack of tools or devices that allow us to see what happens at the polyelectrolyte junction. A monitoring system that can provide information about the mass transport and dynamic distribution of ions at the polyelectrolyte junction in real time would constitute a remarkable breakthrough in this field. Besides, a chip-based integrated ionic circuit may offer a test bed on which various designs can be created and checked, similar to a breadboard used for testing electronic circuits. In this respect, a microfluidic chip has great potential to be a platform for ion-based information processes (iontronics) and biomimicking of neuronal membranes by allowing the functional control and real-time display of ion current; such advantages are demonstrated herein.

We report the first example of a microchip-based polyelectrolyte diode and prototypes of integrated ionic circuits. The components and the structure of the proposed system are shown in Figure 1. Conventional photolithographic techniques were used to fabricate a narrow channel to connect the two reservoirs. Briefly, a pair of ionic polymers, poly(diallyldimethylammonium chloride) (pDADMAC) with a positively charged backbone and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (pAMPSA) with a negatively charged backbone, were synthesized by photopolymerization of the corresponding monomers at the narrowest region by sequential UV exposure through a prepatterned mask. The two reservoirs behind the junction were filled with an aqueous electrolyte solution.

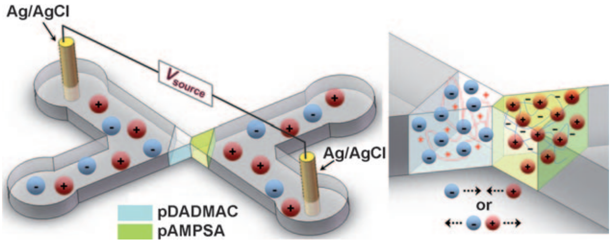

Figure 1. Schematic depiction of a microchip-based polyelectrolyte diode. The polyelectrolyte plugs are shown in transparent blue and green. The ions of the aqueous electrolyte solution in the reservoirs are shown as blue and red spheres. On the right, a close-up view of the polyelectrolyte junction shows the polyanionic nature of pDADMAC and the polycationic nature of pAMPSA.

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[**] This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST) (No. R11-2007-012-02002-0(2009)) and the Korea government (MOST) (No. R01-2006-000-10240-0), the Nano/Bio Science & Technology Program (M10536090001-05N3609-00110) of the Ministry of Education, Science and Technology (MEST), and the Seoul Science Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900045.

An anionic fluorescent dye, fluorescein, was utilized to display the dynamic distribution of ions across a pair of oppositely charged polyelectrolyte plugs. The contrast of green fluorescent emission at the interface (Figure 2a) is sufficiently sharp to visualize the polyelectrolyte junction clearly. The bright fluorescence at the plug on the left-hand side shows that the fluorescein concentration in the positively charged pDADMAC plug is much higher than that in the bulk solution, thus indicating the high charge density of the plug. In contrast, the dark area on the right-hand side reveals that fluorescein molecules are absent in the negatively charged pAMPSA region.

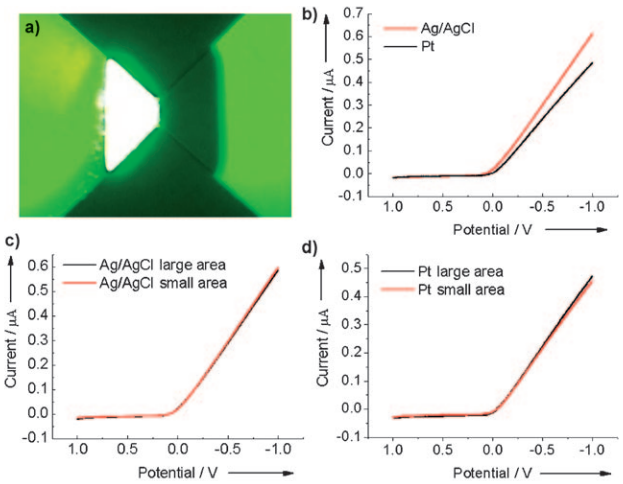


Figure 2. a) A polyelectrolyte diode comprising pDADMAC (left) and pAMPSA (right) on a microchip. The cross-section of the junction is approximately 30 µm deep and 100 µm wide. A 10 mM NaCl solution containing 1 µM fluorescein sodium salt was used. No electric field is applied. b) *I–V* curves in 10 mM NaCl aqueous solution using Ag/AgCl or Pt electrodes. c) *I–V* curves at Ag/AgCl electrodes in 10 mM NaCl aqueous solution for an electrode with a large surface area and for one with a small surface area. d) *I–V* curves at Pt electrodes in 10 mM NaCl aqueous solution for an electrode with a large surface area and for one with a small surface area. Scan rate was 100 mV s^{-1}.

The proposed system was specially designed to ensure that the rectification was free from electrochemical reactions. First, two nonpolarizable Ag/AgCl electrodes were employed to minimize the impedance at the interface between the electrodes and the solutions. Second, the cross-sectional area of the neck-like polyelectrolyte junction was sufficiently narrow to make the electric potential drop predominantly at the polyelectrolyte junction (see the Supporting Information) Figure 2b shows *I–V* curves obtained from the proposed polyelectrolyte diode system. The slopes of both curves are asymmetric; however, the curve obtained using Ag/AgCl electrodes (red) is steeper than that obtained with Pt electrodes (black). Moreover, the onset potentials of the *I–V* curves for the Pt and Ag/AgCl electrodes are almost same and markedly lower than those of reported systems.[5] Figure 2c,d demonstrates that the current is independent of the contact area between the electrodes and the solutions. Owing to the nonpolarizable electrodes and the narrow polyelectrolyte junction, the rectification behavior was minimally affected by electrochemical reactions. Therefore, the well-defined diode-like rectification resulted from an ion current that was completely governed by the nonlinear variation of ionic conductance arising exclusively from the microscale polyelectrolyte junction.

To date, the dynamic distribution of ions in the polyelectrolyte plugs under electric field has remained a point of speculation. In this context, the microchip-based system provides a useful means to visualize the dynamic distribution of ions in real time by employing fluorescent dyes. Figure 3a shows a series of fluorescence images captured when an electric field was applied. Under a forward bias, the anionic fluorescein molecules gradually escape from the junction area in the positively charged pDADMAC phase, while the fluorescence is restored under reverse bias. Although these results appear to contradict what was expected, the presence of an excess of chloride ions in the solution explains this phenomenon (Figure 3b). When a forward bias strongly increases ion concentration at the polyelectrolyte junction, the fluorescein molecules in the pDADMAC phase are replaced by chloride ions. This result is not surprising considering that chloride ions are smaller than fluorescein ions bearing the same charge and are thus expected to more efficiently fulfill the charge requirement that the external

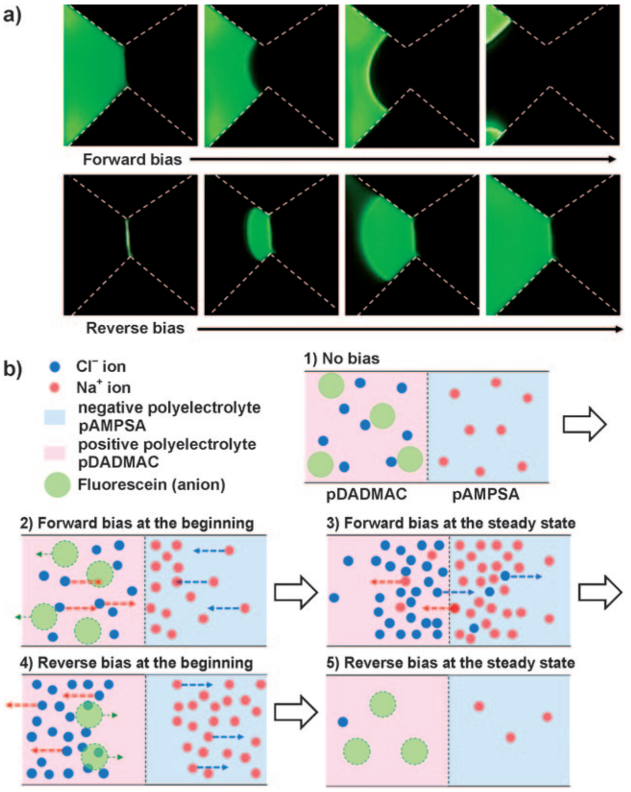
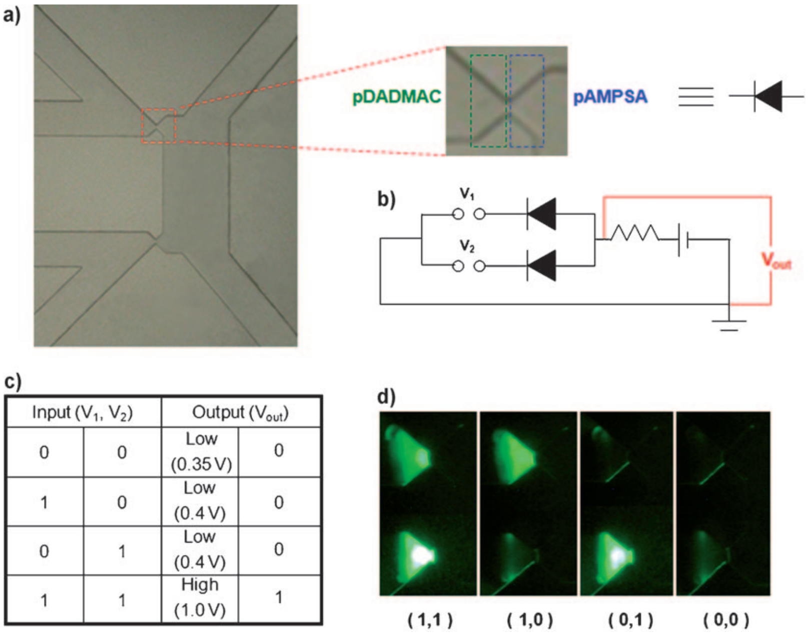


Figure 3. a) Fluorescence images of a pDADMAC region (left) captured every 20 s (forward bias) and 10 s (reverse bias) in a 10 mM NaCl solution containing 1 µM fluorescein under an electric field. b) A schematic view of ion distribution in response to the external electric field.

electric field imposes on the polyelectrolyte junction. When a subsequent reverse bias is applied, ion concentration at the junction is reduced and chloride ions leave the pDADMAC phase starting from the junction area. The reduced but still required negative charge is provided by fluorescein ions rather than chloride ions, thus resulting in the fluorescence recovery. This effect of anionic size can be confirmed by replacing chloride ions with tetraphenylborate (10 mM, as its sodium salt, STPB), which is comparable in size to the fluorescein ion (see the Supporting Information). In contrast to the images shown in Figure 3a, with the STPB electrolyte fluorescein molecules come into the pDADMAC phase under a forward bias, while they are repelled from the polymer phase under a reverse bias. (Figure S3 A)

Polyelectrolyte diodes on a microchip can be patterned and integrated to operate as an "ionic circuit". Figure 4a,b shows the microchip pattern for an AND gate and the corresponding equivalent circuit. The AND gate comprises two pairs of polyelectrolyte plugs. As shown in the truth table in Figure 4c, output (1 V) was regarded as logical 1 when both electric inputs (4 V) were applied. Because inherent resistance of the channel is about 2 MΩ, we can neglect the possibility of electrochemical reaction at the Ag/AgCl electrode when a potential of 4 V is applied. For more examples, we designed and demonstrated OR and NAND logic gates composed of two and three pairs of polyelectrolyte plugs, respectively (see the Supporting Information). Both of these digital logic gates comprising an ionic circuit work properly. In addition to the electrical signals, the fluorescent emission at the polyelectrolyte plugs allows us to optically read the input signals that are applied to the individual diodes in the logic gates. As an example, Figure 4d shows that the on and off states of each polyelectrolyte diode are displayed by light emission, indicating input signals.



Input (V_1, V_2)		Output (V_{out})	
0	0	Low (0.35 V)	0
1	0	Low (0.4 V)	0
0	1	Low (0.4 V)	0
1	1	High (1.0 V)	1

Figure 4. a) A microchip pattern for an AND logic circuit. b) The equivalent circuit of the AND logic gate. c) The truth table of the electrical inputs to and outputs from the chip. d) The fluorescent output images of the AND gate. The input voltages were 4 and 0 V.

In summary, we have developed a microchip-based polyelectrolyte diode. Compared to previous polyelectrolyte diodes, our chip system displays significantly improved rectification that is exclusively controlled by the ionic conductance across the polyelectrolyte junction, and the dynamic distribution of ions can be visualized on a real-time basis using fluorescent ions. More interestingly, a variety of logic gates can be fabricated by integrating multiple polyelectrolyte diodes on a microchip; we also constructed light-emitting logic gates that optically and simultaneously display the applied input signals. We believe that the proposed microchip-based polyelectrolyte system may open new avenues of research and suggest novel applications, such as monitoring the dynamic distribution of specific ions at interfaces in a layer-by-layer membrane system, developing more advanced iontronics, and producing intelligent chip devices that can mimic the nonlinear functions of biological systems, for example, asymmetric neuronal signaling across cell membranes.

Experimental Section

Materials: All chemical reagents were used without further purification. Diallyldimethylammonium chloride (DADMAC), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), sodium chloride, potassium chloride, 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator), sodium tetraphenylborate (STPB), 3-(trimethoxysilyl)propylmethacrylate (TMSMA), methanol, fluorescein, platinum foil (0.05 mm thick, 99.9 %), and Ag wire (0.5 mm thick, 99.9 %) were purchased from Aldrich.

Microchip fabrication and preparation of polyelectrolyte junction: The microchips were fabricated largely following the reported procedure.[12] The procedure is described in more detail in the Supporting Information.

Electrochemical and optical measurements: The *I*–*V* curves were plotted using an electrochemical analyzer (CH750, CH Instruments Inc., USA). The electrolyte (NaCl) concentration was 10 mM. The Ag/AgCl wires in each of the reservoirs were connected to an electrochemical analyzer. For light-emission experiments, 4 V was applied across the polyelectrolyte diode to bring about a rapid variation in fluorescence. The fluorescence intensity was measured by a fluorescence microscope (TE2000U, Nikon, Japan).

Experiments for logic gates: The electrical outputs were recorded by a multimeter (Fluke 187, Fluke, USA), and the electrical inputs to the polyelectrolyte diode were applied using two or three DC power supplies (XDL 35–5P, Xantrex Inc., England).

Received: January 5, 2009
Revised: February 21, 2009
Published online: April 17, 2009

Keywords: fluorescence · ionic circuits · microchips · polyelectrolytes · rectification

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