Polyelectrolyte Diode: Nonlinear Current Response of a Junction between Aqueous Ionic Gels

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Abstract: We demonstrate that a fixed junction between two aqueous gels containing oppositely charged polyelectrolytes could rectify electric current. The agarose-based gels were "doped" with sodium poly-(styrene sulfonic acid) and poly(diallyl dimethylammonium chloride). The unidirectional current response of the interface between the cationic and anionic gels originates directly from anisotropy in the mobile ionic charges in the gels. The current depends on the concentration of polyelectrolyte, the background ionic concentration, and the distance traveled by the ions. The $I-V$ curves from the devices demonstrated a combination of transient and stationary rectification effects. The current densities achieved were comparable to or higher than those obtained with previously reported organic semiconductor diodes. The diodes had good long-term stability in both DC and AC conduction modes. The materials and the process of preparation of these devices are simple, inexpensive, and scalable. They could be used in flexible and biocompatible electronic circuits.

Introduction

Silicon and other inorganic semiconductors are the predominant materials in electronic manufacturing today; however, the development of organic-based electronic components has been a focus of intensive research and development. Organic electronics are not likely to surpass soon the Si-based microcircuits in terms of density of element integration and switching speed, but they have other potential advantages over traditional silicon-based junctions.[1-4] Organic materials have vast potential for integration in low-cost microelectronic devices. Circuits and displays based on organic electronics may also be flexible, low-weight, and environment-friendly. Last, but not least, some water-tolerant organic devices may be biocompatible, that is, they may be used in circuits that directly reside on or are implanted inside animal and human tissue and could perform various sensing, interfacing, and controlling functions for drug delivery, prosthetics, and neural-electronic integration.

Large research effort and significant progress have been achieved in the area of electronics based on conductive polymers. Since their discovery,[5-7] conductive polymers have been used extensively to create organic p-n junctions in solid-state devices analogous to silicon-based electronic p-n junc-tions.[8-16] Conductive polymer junctions are formed in transient[9,10] or fixed state using frozen-junction,[11,12] electrochemical disproportionation and trapping methods[14] or radical-induced polymerization of ion-pair monomers as counterions.[15] The conductive polymers can be doped by using, for example, ion implantation.[17] The unidirectional current response of these polymeric junctions can be based on redox reactions occurring either across a membrane[18] or at the interface with the electrodes.[19,20]

As an alternative to electronic current carriers, a few articles report the fabrication and properties of organic rectifying junctions where the current is carried by ions. For example, Bernards et al. have used two organic semiconductors with mobile anions and cations to create an interface across which the ionic current flows unidirectionally.[21] The ions that carry the current can result from electrolyte dissociation in water.[22]

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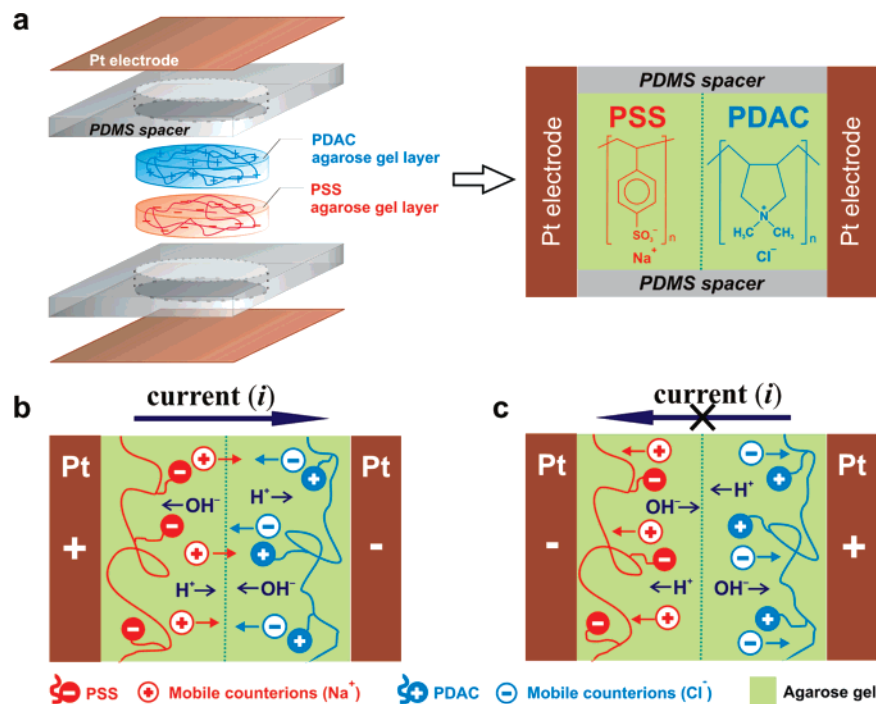
Figure 1. (a) Schematic of the gel diode device. Two slabs of aqueous agarose gels containing oppositely charged polyelectrolytes and corresponding counterions are sandwiched between platinum electrodes and sealed by PDMS spacers. Schematic of the ion migration in the gel diode (b) at forward bias and (c) at backward bias.

The ionic conductance between chambers containing electrolytes in water can be controlled by "bipolar membranes" with cationic and anionic sides allowing directional ionic transport of the electrolyte solution in which they are immersed.[23,24] Alternatively, in the so-called "electrolyte diode",[25-27] a uniform hydrogel or ion-permeable membrane separates two reservoirs containing acidic and basic solutions. In the forward voltage, the ions cross the membrane moving toward the electrode of opposite sign. In the backward direction, only hydroxide and hydrogen ions enter the membrane where they combine to form water and dramatically decrease the local conductivity. The bipolar membranes and electrolyte diodes, however, are not practical as they include water-filled chambers. In addition, their operation may be dependent on the existence of gradients of electrolyte and/or pH, which may level out over time, at which point these devices will stop rectifying.

We demonstrate here the formation of a fixed rectifying junction between two aqueous gels containing oppositely charged polyelectrolytes. These diode prototypes operate on the (counter) ionic conductance in the gels. The anisotropic distribution of positive and negative mobile counterions within the device leads to nonlinear current conduction across the gel junction. Remarkably, these "soft" diodes operate on the basis of very simple and inexpensive waterborne gels and polyelectrolytes. The matrix of the gels is agarose, a gelling agent widely

used in biotechnology and food industry. Two typical polyelectrolytes, sodium poly(styrene sulfonic acid), PSS, and poly-(diallyl dimethylammonium chloride), PDAC, are used to dope the gels.

Experimental Section

Materials. Poly(styrene sulfonic acid), sodium salt (MW 70 kDa), and poly(diallyl dimethylammonium chloride) (MW 400−500 kDa) were purchased from Polysciences Inc. and Aldrich, respectively. Agarose (biochemistry research grade) was obtained from Acros Organics. Milli-Q water was obtained from Millipore RiOs 16 reverse osmosis water purification system. Platinum foil (99.9%, 0.025-mm thick) used as electrodes was purchased from Alfa Aesar. Gold electrodes were prepared on precleaned glass microscope slides by depositing 10 nm of chromium followed by 100 nm of gold in a metal evaporator (model FPS2-41, Cooke Vacuum Products).

Preparation and Characterization of Gel Diodes. PSS solutions (3.5, 7.0, and 14.0 wt %) and PDAC solutions (2.5, 5.0, and 10.0 wt %) were prepared separately with Milli-Q water under continuous stirring. Agarose (2.0 wt %) was added to two oppositely charged polyelectrolyte solutions, and the mixtures were boiled on a hot plate under continuous stirring. For gelation of the solutions, the mixtures were cooled to room temperature under gentle stirring to avoid bubble formation. Cylindrical slabs of 5-mm diameter were cut from the agarose gels containing the polyelectrolytes and desalinated for varying periods of time in large vessels with Milli-Q water. Poly(dimethylsiloxane) (PDMS) spacers were prepared from Sylgard 184 (Dow Corning) with 0.5-, 0.9-, 1.0-, and 1.25-mm thickness and punched to make a 5-mm diameter hole. The PDMS spacers were placed on platinum or gold electrodes, and cylindrical slabs of the gels were inserted into the hole of PDMS spacers. Both agarose gels confined on the metal electrodes (first gel containing PSS and second gel containing PDAC) were then brought in contact with each other, creating the gel interface, and clamped (Figure 1).

The current−voltage characteristics of the device were measured with various sweep scan rates (50, 100, 250, and 500 mV/s) by using a computer-controlled source meter (Keithley 2602, Keithley Instru-

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ments Inc.) and probe station (Janis Research Co. Inc.) at room temperature. The temporal current responses of the gel diode under continuous application of constant voltage were measured by using a DC regulated power supply (Extech Instruments) and a digital multimeter (34405A, Agilent Technologies). The transient response measurements were performed by using a function generator (33120A, Agilent Technologies), computer-controlled digital oscilloscope (DSO3202A, Agilent Technologies), and digital multimeter.

Results and Discussion

The diodes were formed by bringing in contact two gels containing high molecular weight polyelectrolytes of opposite charges (Figure 1a). Initially, the gelled aqueous phases were desalinated in Milli-Q water to remove the excess (background) electrolyte ions in the system. The high molecular weight polyelectrolytes are trapped in the gel matrices of the device and cannot migrate. Thus, the polyelectrolyte counterions as well as the hydroxide and hydrogen ions from dissociation of bulk water are the only charged species that can transport the current across the junction when an electric field is applied. In the forward direction (positive electrode in contact with PSS gel layer, negative electrode in contact with PDAC gel layer), the polyelectrolyte counterions move toward the opposite electrodes crossing the interface, thus conducting current (Figure 1b). On the other hand, in the backward direction the counterions are attracted to the nearest electrode and do not cross the interface between the two gel layers, creating a depletion region around the junction (Figure 1c). Only minor amounts of hydrogen and hydroxide ions present in the system migrate toward the gel interface and associate to form water near the junction.

We confirmed that the asymmetric interface between two oppositely charged gel polyelectrolytes was essential in forming a rectifying junction by comparing the current response from our device to ones from two non-doped agarose gels or combinations of one charged gel containing polyelectrolyte and one pure non-doped gel. The current–voltage curve for two pure agarose gels was symmetric about zero bias, and the rectification ratio (the ratio of current at +5 V to current at −5 V) was near unity (Figure 2a). Additionally, no rectification was observed when only one of the gels contained either of the polyelectrolytes. The *I*–*V* curve of a device interfacing a gel layer containing PSS (7.0 wt %) with a pure agarose gel was symmetric about zero bias, and the rectification ratio was unity. We recorded a slight rectification effect with the gel combination involving a pure agarose gel and another one containing PDAC (5.0 wt %); however, this is possibly because the pure agarose gel is slightly anionic[28] and forms an asymmetric interface with the positively charged PDAC (Figure 2a). Junctions prepared with oppositely charged polyelectrolyte in the two gels forming the interface, however, showed pronounced current rectification. As the concentrations of polyelectrolyte dopants within the gel phases were increased, the rectification of the device was enhanced as a result of a higher counterion concentration being available for conducting the current across the gel interface (Figure 2b).

We monitored the current response from several devices prepared from gels desalinated for various times to study the role of counterionic current transport. The desalination procedures result in junctions containing decreasing amounts of

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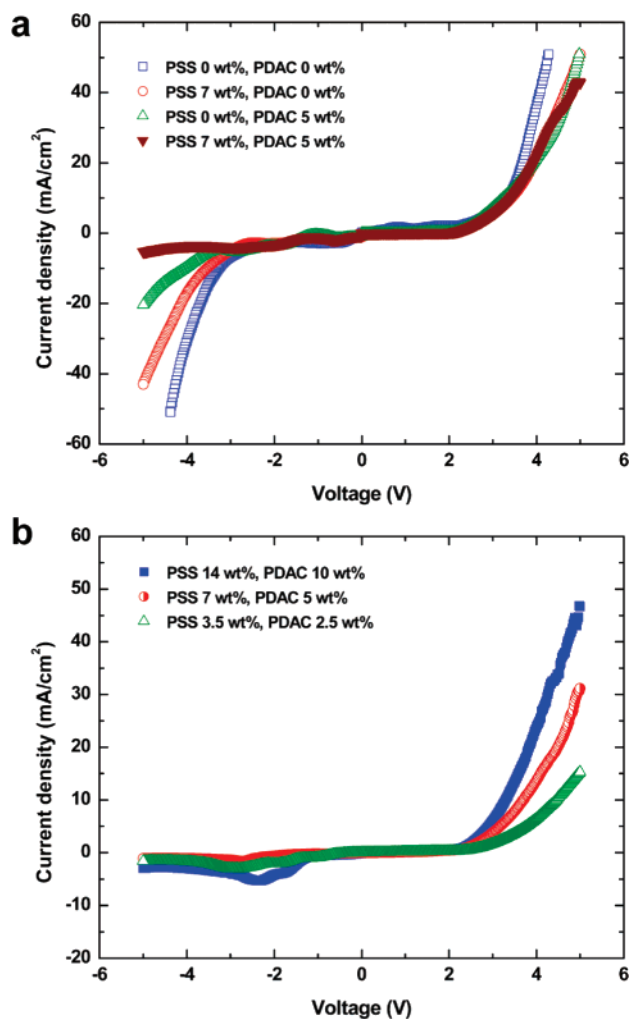
Figure 2. (a) Current density as a function of applied bias for junctions prepared from different gel combinations. Each gel layer was 1-mm thick and was desalinated for 2 h in DI water except for the pure agarose gel layer, which was used without desalination. The *I*−*V* curves demonstrate that only junctions prepared from two oppositely charged polyelectrolyte gels show significant current rectification. (b) Current density as a function of applied bias for junctions prepared from agarose gel layers containing different amounts of polyelectrolytes. Each gel layer was 1-mm thick. All gels were desalinated for 90 min in DI water. Sweep scan rate was 100 mV/s.

background electrolyte. Indeed, as the desalinating time of the gels increased, the overall conductivity of the device decreased (Figure 3a). However, the current rectification ratio was enhanced as the current in the backward direction was dramatically reduced compared to that in the forward direction (Figure 3b). Clearly, the removal of extra background ions significantly improves the rectification of the devices, which demonstrates that the rectification effect is dependent on the oppositely charged counterions surrounding the polyelectrolyte molecules in the two gel layers and is suppressed by the presence of arbitrary electrolyte ions. Additionally, in unwashed gels electrochemical reactions of the contaminant salts at the electrodes also led to a peak in backward current density (Figure 3a). This characteristic peak was progressively removed after the gel phases were desalinated. Different electrode materials were tested to minimize this effect, and platinum was found to be the less reactive electrode material in this particular system (Supporting Information Figure S1). Importantly, varying the electrode metal type did not influence the capability of the
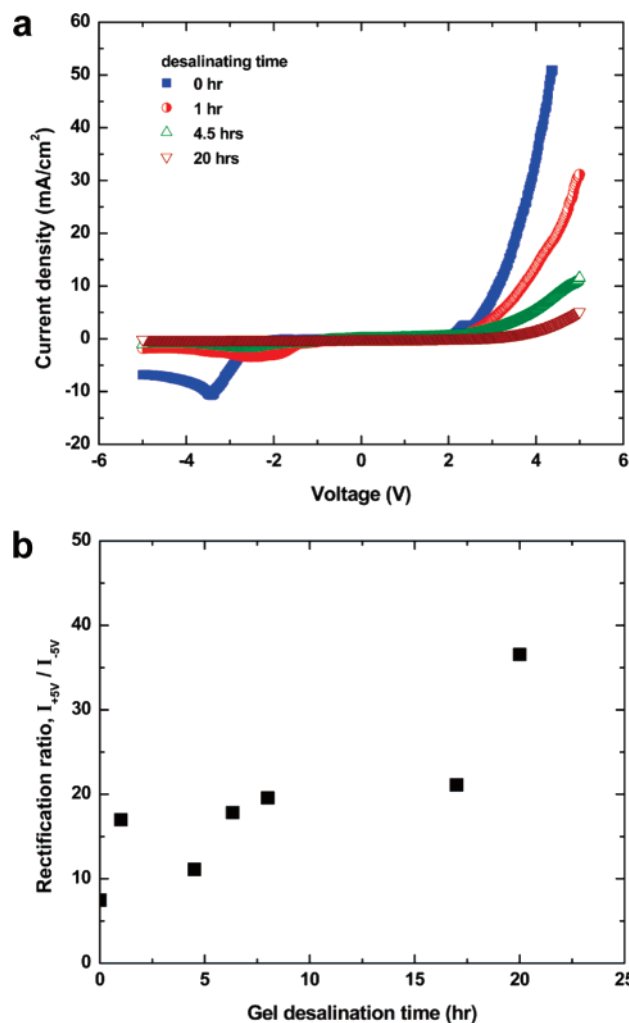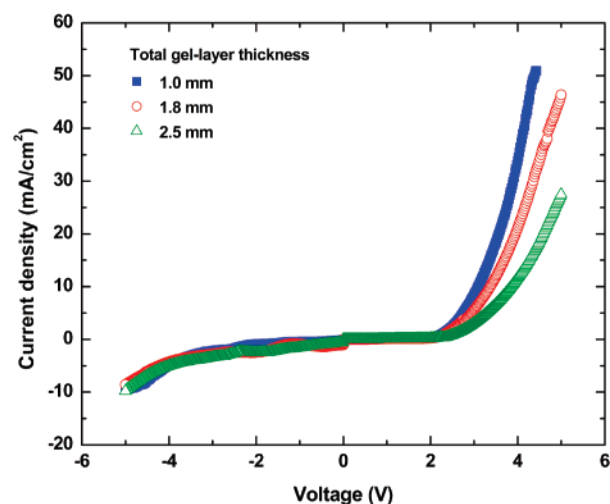
Figure 3. (a) Current density as a function of applied bias for a gel diode junction after different desalinating times. The two gel layers contained 7.0 wt % PSS and 5.0 wt % PDAC in 2.0 wt % agarose gel and were 1-mm thick. Sweep scan rate was 100 mV/s. (b) Current rectification ratio at ±5 V under forward and backward biases as a function of the gel desalinating time. Although the overall conductivity of the gel diode decreases with increasing gel desalinating times, the current rectification ratio is significantly improved.

devices for current rectification. Hence, we believe that the rectification effect is primarily a result of the counterionic current and interactions in the gel system rather than electrochemical reactions occurring at the electrode−gel interface.

We measured current rectification ratios between forward and backward directions as large as ∼40 and current densities up to 50 mA/cm^2 (potentially even higher densities could be achieved; however, instrumental limitations prevented us from measuring higher currents as apparent in Figure 3a). Our gel diodes showed current densities higher than those usually reached by ionic junctions (typically in the range of 0.1−10 mA/cm^2),[24,27] although this parameter has been measured at different voltages by different researchers. Thus, the gel diodes presented in this report can help bring the characteristics of organic diodes based on ionic current carriers closer to ones of devices built from conductive polymers. Indeed, the highest current density value of the gel diodes was comparable to some of the diode junctions made from polymeric films.[8,10,12,14,16]

Gel diodes of different thicknesses were fabricated to evaluate the effect of distance between the electrodes (spanned by the
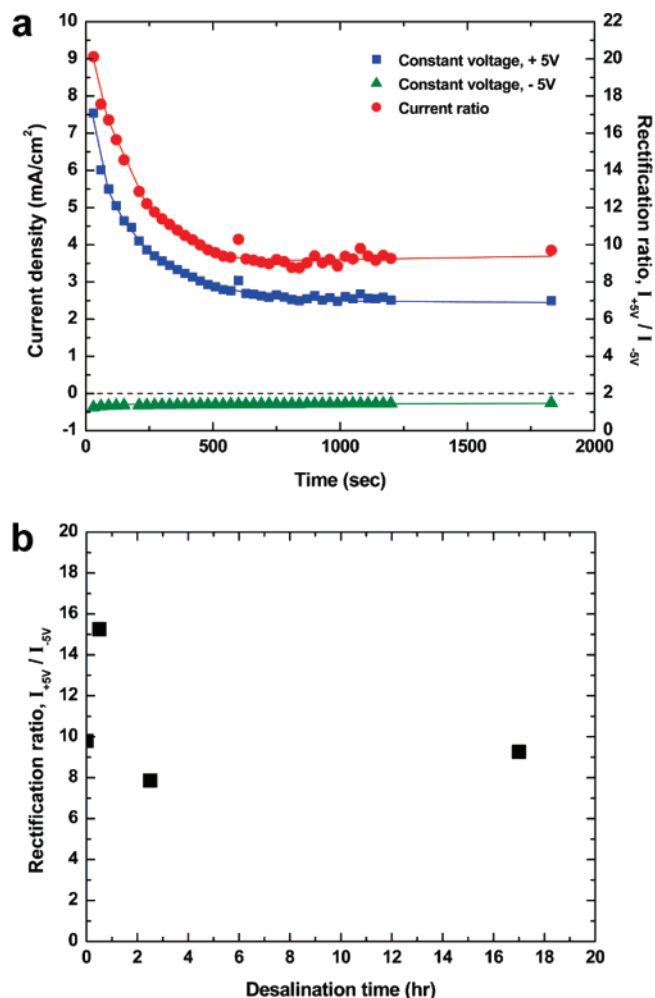
Figure 4. Current density as a function of applied bias for gel diodes of different thicknesses. The two gel layers contained 14.0 wt % PSS and 10.0 wt % PDAC in 2.0 wt % agarose gel and were desalinated for 2 h in DI water. Sweep scan rate was 100 mV/s. The current increase in forward bias for thinner devices is a consequence of smaller distances of migration for the counterions resulting in higher electric field strength across the gel interface. The depletion region around the gel interface due to the formation of water and motion of the counterions toward the electrodes results in low currents independent of the device thickness for backward bias. Note that in the case of the thinner device the current densities measured reached 50 mA/cm^2 before the final +5 V voltage; one can assume that higher current densities can therefore be achieved.
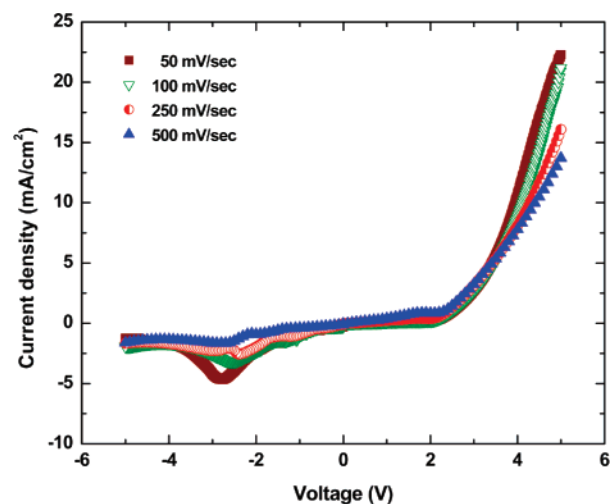
Figure 5. Current density measured at different sweep scan rates as a function of applied bias for a diode junction composed of two gel layers containing 7.0 wt % PSS and 5.0 wt % PDAC in 2.0 wt % agarose gel. Each gel layer was 1-mm thick and was desalinated for 2 h in DI water.

ionic current carriers) on the rectification and conductivity of the devices (Figure 4). As expected, the conductivity of the diodes in the forward direction increased when the total device thickness decreased. This can be attributed to a smaller distance of migration toward the opposite electrode for the counterionic current carriers and a reduced resistance in thinner gel slabs. However, the conductivity in the backward direction was independent of the gel thickness. This result agrees with the development of a depletion region around the gel junction where conductivity drops to very low values because of migration of the counterions away from the interface toward the electrodes and the formation of water as hydrogen and hydroxide ions associate when meeting in the vicinity of the junction.
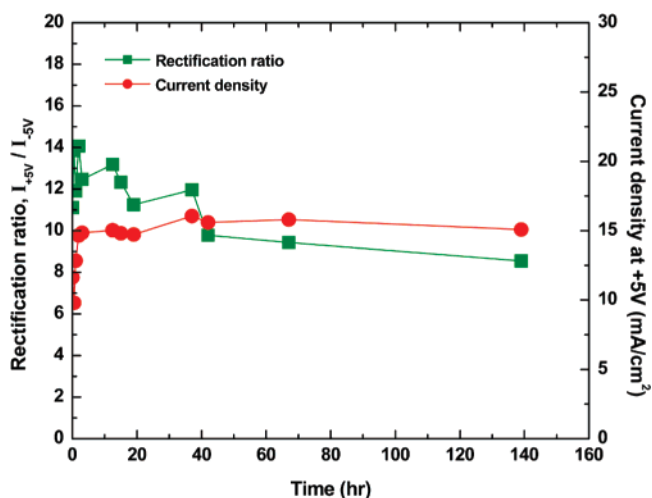
Figure 7. Time dependence of current rectification ratio and current density for a typical diode composed of two layers containing 7.0 wt % PSS and 5.0 wt % PDAC in 2.0 wt % agarose gel. Each gel layer was 1-mm thick and was desalinated for 5 h in DI water. The currents through the system were measured with DC sweep scanning. The diodes showed stable current response and stable rectification ratio for more than a week.
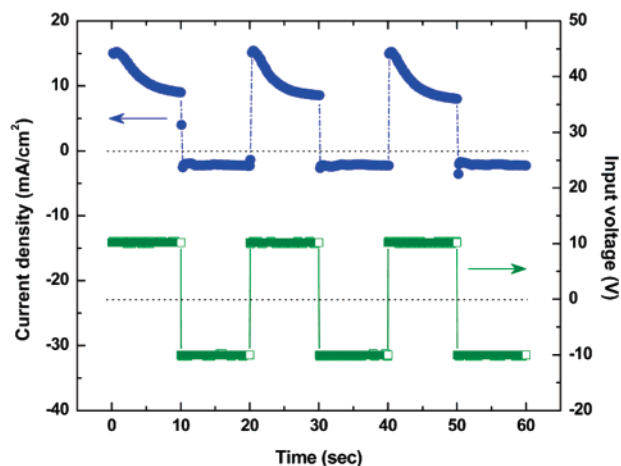

Figure 6. (a) Time dependence plot of current density and current rectification ratio from a typical gel diode at constant forward (+5 V) and backward (−5 V) bias. Under continuous application of constant voltage across the junction, the currents in both directions stabilized rapidly and then remained constant. (b) Current rectification ratio at 30 min after voltages of ±5 V with different desalination times were applied. For both plots, the gel diode was constituted of two gel layers containing 7.0 wt % PSS and 5.0 wt % PDAC in 2.0 wt % agarose gel. Each gel layer was 1-mm thick and the gels in (a) were desalinated for 17 h.

Figure 8. Current response of a gel diode under AC field of 50 mHz. The oscillogram of the voltage applied is plotted on the bottom. Two gel layers contained 7.0 wt % PSS and 5.0 wt % PDAC in 2.0 wt % agarose gel. Each gel layer was 1-mm thick and was desalinated for 19 h in DI water.

This hypothesis is also supported by the data for the current responses from the same gel diode for various sweep scan rates presented in Figure 5. When scanning in forward bias, lower currents were recorded at +5 V as the scan rate was increased, which shows that the system has not yet reached steady state, as expected for a junction based on ionic current. The final current densities at −5 V (Figure 5) and the current responses for backward bias of the more desalinated gel layers (Supporting Information Figure S2) were independent of the scan rate. This also points out that a depletion region is forming around the gel interface as the polyelectrolyte counterions do not act as current carriers in this direction. In addition, the current peak in the backward bias due to electrochemical reaction was gradually suppressed as the sweep rate was increased. This is possibly due to a suppressed diffusion of reactive ions toward the electrode surfaces at high sweep scan rate. Furthermore, the current response of gel diodes showed hysteresis resulting from the low ionic mobility (Supporting Information Figure S3).

In all measurements presented above, a part of the current response of the gel diodes is transient and thus depends on the

sweep rate. To investigate how long our devices require to reach steady state, we performed measurements of the long-term current response as a function of time at constant forward (+5 V) and backward (−5 V) bias. The current response was found to decrease rapidly in the first 500 s for both biases and then stabilize at a nearly constant value in less than 1 h. Once constant current values were reached in both directions, the current ratio for a bias of ±5 V stabilized at a value around 10, hence conserving the rectification effect of the gel diode (Figure 6). These experimental data demonstrate that the gel diodes can operate in DC mode for long periods and that the rectification effect is not gradient-driven and largely results from a stationary currents directly due to the charge anisotropy within the system. We also proved that the devices have long-term stability by monitoring their current response for several days with DC sweep scanning (Figure 7). The current density and current rectification ratio at ±5 V between forward and backward direction were found to be stable for more than a week as long as the gels were prevented from drying.

The transient and steady-state current responses of the gel diodes were also investigated with an alternating electric field applied across the gel interface. The corresponding current response of the gel diodes was recorded in real time. The gel diode displayed good rectification of the input AC voltage for frequencies under 1 Hz (Figure 8). For each voltage cycle, the data curves display a small stationary current during the periods of voltage in backward bias and a large decreasing current in forward bias. The pronounced relaxation after change from backward to forward bias possibly is a result of a transient, diffusion-controlled response to the suddenly switched voltage. Nevertheless, even after the current response leveled off in the forward bias of one cycle, the devices exhibited a strong rectification effect. In the same manner as the effect recorded for a DC sweep, the rectification ratio rapidly decreased from an initial high value to a stationary one, which was then found to be stable for many cycles (at least 30). The dynamic long-term performance of the gel diodes will require additional studies, but the data presented here appear very encouraging for potential application of such devices in electronic circuits.

The exact physical mechanisms of operation of the gel diodes are still not characterized in detail in terms of ionic transport and reactions at the junction and at the electrodes. It is likely that electrolysis of water without visible release of gas is involved in the steady-state current transfer at the electrodes. It is important, however, that we have proved that the asymmetric conductance does not seem to arise from gradients in the ionic concentration. Even though this is the mode of operation of the previously reported electrolyte diodes,[25,27] it can be argued that a true rectifying junction would not become depleted upon continuous application of constant voltage across the junction under both forward and backward bias. The existence of a large stationary part of the current and the long-term stability point out that this may be the case with the gel devices reported here.

Conclusions

We demonstrated that current-rectifying diode junctions can be fabricated by interfacing aqueous gels doped with oppositely charged polyelectrolytes. The remarkable feature of these rectifying junctions is that they operate on the basis of water-borne ions. These devices combine the ionic current rectification of electrolyte diodes and the stability and ease of fabrication of polymer electronics. Electronic components based on organic materials are of interest because they possess a number of potential advantages over traditional silicon-based junctions. Even though our devices were first-generation prototypes without any optimization, the gel diodes had comparable or higher current density and rectification ratios than other organic-based electronic counterparts. The process of their preparation is simple, environment-friendly, and scalable. These devices are potentially good candidates for facile integration in biomimetic electronic devices and circuits. The gel and other components that constitute them are flexible and inexpensive. Because the gel diodes are based on aqueous media, they could be used in bioelectronic devices. These principles could be extended to gel transistors and other equivalent electronic elements.

Supporting Information Available: Additional experimental data on the effect of electrode materials on the current response for gel diode, current response at varying sweep scan rates, and current hysteresis in the device. This material is available free of charge via the Internet at http://pubs.acs.org.

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