Ionic Current Rectification in Soft-Matter Diodes with Liquid-Metal Electrodes

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A soft-matter-based diode composed of hydrogel and liquid metal (eutectic gallium indium, EGaIn) is presented. The ability to control the thickness, and thus resistivity, of an oxide skin on the metal enables rectification. First, a simple model system with liquid-metal/electrolyte-solution/Pt interfaces is characterized. The electrically insulating oxide skin on the EGaIn electrode is reduced or oxidized further depending on the direction of the bias, thereby allowing unidirectional ionic current. The forward current of the diode increases as the conductivity of the electrolyte increases, whereas backward current depends on the pH of the medium in contact with the insulating oxide layer on the EGaIn electrode. As a result, the diode shows a higher rectification ratio (defined as the ratio of forward to backward current measured at the same absolute bias) with more conductive electrolyte at neutral pH. Replacement of the liquid electrolyte solution with a hydrogel improves the structural stability of the soft diode. The rectification performance also improves due to the increased ionic conductivity by the gel. Finally, a diode composed entirely of soft materials by replacing the platinum electrode with a second liquid-metal electrode is presented. Contacting each liquid metal with a polyelectrolyte gel featuring different pH values provided asymmetry in the device, which is necessary for rectification. A hydrogel layer infused with a strong basic polyelectrolyte removes the insulating oxide layer, allowing one interface with the EGaIn electrode to be conductive regardless of the direction of bias. Thus, the oxide layer at the other interface rectifies the current.

1. Introduction

There has been increasing interest in soft devices inspired by biological systems.[1–3] Various types of devices made of soft materials, such as polymers, gels and liquids, have been constructed including diodes,[4,5] transistors,[6–10] antennas,[11–13] sensors,[14] actuators,[15,16] batteries,[17,18] supercapacitors,[19,20] memristors,[21] and solar cells.[22,23] Soft materials are appealing because they can be stretchable, flexible, and conformal. Due to their ease of physical deformation, devices made of soft materials could find potential applications that include portable or wearable electronics and bioprosthetic devices such as artificial organs,[24] muscle,[25] neural tissue or skin.[14,26,27] We describe the operating principles of a new class of diodes constructed entirely from soft materials such as hydrogels infused with electrolytes and liquid-metal electrodes.

Directional conduction of an ionic current is one of the key processes in many essential biological functions, such as adenosine triphosphate (ATP) synthesis and neural transmission. Our group reported previously ionic current diodes made of soft, aqueous gel operating on ionic current. One approach is based on an interface between two hydrogel layers doped with differently charged polyelectrolytes that is analogous to the p–n junction of a Si diode.[4] A SiO_2 nanofilm/aqueous gel interface (SNAGI) shows ionic current rectification due to the electrostatic gating of the negatively charged SiO_2 nanolayer.[5] In these gel-based diodes, a network of agarose polymer provides the physical matrix that allows the liquid media to be confined and shaped. Although the gel materials are soft and flexible, the rigid electrodes used in those devices, such as platinum, fluorine-doped tin oxide (FTO) glass and highly doped Si wafers make the overall device rigid. Replacement of the solid electrodes with soft metallic material is required for making a truly soft diode.

Eutectic gallium indium (EGaIn), an alloy of 75% gallium and 25% indium, could be an alternative to the rigid electrodes commonly used to interface gels since it is a low viscosity liquid at room temperature and has high electrical conductivity ($\sigma = 3.4 \times 10^4$ S cm^{-1}). Electronic devices such as stretchable antennas,[11–13] interconnects,[28–30] electromagnets,[31] micro-components,[32–35] and reconfigurable wires[36] have been fabricated utilizing the fluidic properties of low melting point metal alloys. The surface of EGaIn spontaneously forms a thin, native skin of gallium oxide.[37] The oxide skin passivates the liquid metal and does not grow with time unless an external driving force is applied (e.g., temperature, electrical potential).[38] The oxide layer is less conductive than the metal (pure, crystalline gallium oxide is a wide band gap semiconductor), and can be formed or removed by the applied bias. This property makes it possible to construct resistive switching memory devices, in which the state of the resistance can be recorded in the form of the thickness of the oxide.[21] We report here how the ability

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to control the thickness of the oxide layer on the liquid metal could be used to achieve electrical rectification in a novel class of soft-matter diodes composed of liquid metal and hydrogel. Similarly, anodic oxide films of valve metals (e.g., Ta, Zr, Ti and Al) have been reported to show current rectification in dry (metal/oxide/metal) or wet (metal/oxide/electrolyte) conditions.[39] However, the typical valve metals are rigid and the current rectifying mechanism of the metal oxides is derived from their semiconducting characteristics rather than the varying thickness of the oxide films.

The new class of ionic current diodes is made entirely of soft matter by interfacing hydrogel with EGaIn electrodes. First, we investigate the rectification of ionic current at the interface of EGaIn/aqueous electrolyte solution/Pt as a model system. The thickness of the oxide skin at the EGaIn/aqueous electrolyte interface controls the resistance through the device. The ionic current flows in the direction of the bias reducing the oxide skin on EGaIn, while an oxidizing bias suppresses the current. We characterize the effect of the conductivity and pH of the electrolyte solutions on the rectification ratio of the devices. We then demonstrate that replacing the aqueous electrolyte solution with hydrogel (EGaIn/hydrogel/Pt) improves the rectification ratio and enables easy handling and thus practical fabrication of devices. Finally, we discuss the fabrication of diodes composed entirely of soft materials (EGaIn/hydrogel 1/hydrogel 2/EGaIn) by stacking two polyelectrolyte gel layers with different pH to create the necessary asymmetry for rectification.

2. Results and Discussion

2.1. Ionic Current Rectification at the Interface of EGaIn/Electrolyte/Pt

We first investigated a simple model system consisting of EGaIn/electrolyte solution/Pt. A representative current–voltage (*I*–*V*) trace of the system is shown in **Figure 1**. We define forward and backward biases as the negative and positive biases applied to the EGaIn electrode, respectively. The current is suppressed between 0 to –3 V, but increases rapidly at potentials more negative than –3 V. In contrast, positive biases show a continuous and gentle increase in the magnitude of the current. The absolute value of the current at –5 V is ten times higher than that at +5 V. Such diode-like characteristics of the system result from the formation or removal of the insulating oxide film at the interface between the EGaIn electrode and the electrolyte solution.[21] Negative bias applied to the EGaIn electrode reduces the resistive oxide on the surface of the EGaIn electrode, and thus renders the EGaIn/electrolyte solution interface more conductive. The formation and removal of the oxide skin is apparent to the naked eye. In the absence of the resistive oxide skin (i.e., at potentials more negative than –3 V), the current increases noticeably and bubbles form on the EGaIn surface, presumably due to the electrolysis of water. Since the standard reduction potential of the oxide film is about –1.0 V versus SHE (standard hydrogen electrode),[40] the hydrogen generation is supposed to occur prior to the reduction of the oxide during the negative bias sweep. However, the oxide film passivates the EGaIn electrode, thereby hindering the supply of protons to the electrode for the hydrogen generation reaction. The current at positive potentials is likely due to the thickening (i.e., anodizing) of the oxide layer. The oxide layer acts as an insulating barrier, retarding electrochemical reactions such as water electrolysis and further growth of the oxide layer. The inert Pt electrode on the other side does not form any oxide film on its surface and hence stays conductive in this bias range from –5 V to +5 V. Thus, the asymmetric configuration of the reversibly anodizable EGaIn electrode and inert Pt electrodes provide ionic current rectification.

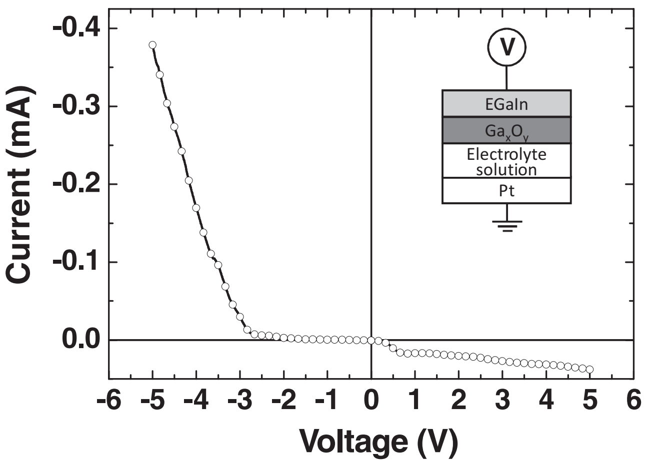

Figure 1. Current rectification of an EGaIn/electrolyte solution (aq)/Pt diode. The experimental setup is shown in Figure S1 in the Supporting Information. The negative (forward) bias reduces the insulating oxide layer at the interface of the liquid metal. The positive (backward) bias oxidizes the liquid metal resulting in a resistive barrier for electrical current. The electrolyte is NaH_2PO_4/Na_2HPO_4 buffer solution with a conductivity of 3.2 mS cm^{-1}.

To elucidate the effect of the electric potential on the formation/reduction of the oxide film on the EGaIn electrode, we observed the surface of an EGaIn electrode in water while changing the applied bias (**Figure 2**) relative to a grounded Pt electrode. We used deionized water as medium to understand the general behavior of the diode in aqueous systems excluding the effect of different types and concentrations of electrolyte ions. The surface of the electrode looks slightly hazy before

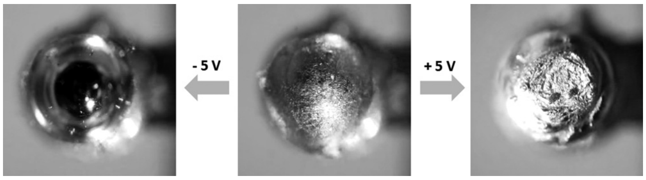

Figure 2. Top-down optical microscope images of an EGaIn liquid-metal electrode of a diode comprised of EGaIn/H_2O/Pt before (middle) and after (left and right) applying biases. The surface of the liquid metal is oxidized or reduced by applying +5 V or –5 V, respectively. The schematic of the experimental setup is shown in Figure S1 in the Supporting Information.

applying bias because of the spontaneous formation of a native oxide skin. Applying a positive bias of +5 V to the EGaIn electrode causes haziness and crumbling on the surface due to the oxide film thickening (see the Supporting Information, Video V1). After applying the positive bias for a couple of seconds, however, we observe no further changes in the morphology of the oxide layer, which is consistent with our hypothesis of the self-limiting oxide growth for the backward current in Figure 1. Applying a negative bias to the electrode causes it to become shiny and reflective, which suggests the metal surface is nearly free of the oxide film (see the Supporting Information, Video V2). The negative bias first reduces the oxide skin, and then generates bubbles presumably due to the electrolysis of water. The observations in Figure 2 confirm the hypothesis that the formation/reduction of the insulating oxide skin on the EGaIn electrode depends on the direction of the electric bias, thereby leading to the unidirectional ionic current characteristics of the EGaIn/electrolyte solution/Pt diode shown in Figure 1.

The time-dependent current response of the EGaIn/H_2O/Pt diode under repetitive application of a positive or negative bias shows clearly the electrochemical characteristics of the oxide film on EGaIn under the backward and the forward bias (**Figure 3**). Application of a positive (backward) bias to the EGaIn electrode immediately generates large current resulting from the formation of the oxide film (Figure 3a). However, since this oxide film retards the ion transport for further oxide buildup, the current decreases by more than an order of magnitude within ten seconds. After a short period (~20 s) with no applied bias, the current remains suppressed upon reapplying the bias, which indicates that the thickened oxide film is maintained even upon removal of the bias. Application of a negative bias to the EGaIn electrode reduces the oxide film and water electrolysis occurs at the interface, which results in a higher current relative to the positive bias (Figure 3b). Under a continuous bias, the forward current is sustained ~10 times higher than the backward current (Figure S2 in the Supporting Information). Turning off the negative bias creates a pulse of positive current, presumably due to the regeneration of the native oxide skin. The current from spontaneous oxidation decays by about an order of magnitude after ~30 s. Based on the derivative of the current with time, the rate of the spontaneous formation of the oxide film on the pristine EGaIn electrode is ~40 times slower than that of the forced oxidation with +3 V bias as shown in the first cycle of Figure 3a. Moreover, the integrated current from the generation of native oxide is smaller than the integrated current from the growth of oxide with applied bias, which suggests that the native oxide without electric bias is thin relative to the oxide grown by positive bias. We observed visually the spontaneous formation of the oxide skin after turning off the negative bias (c.f., Figure 2). Thus, the oxide formation on the EGaIn electrode is a spontaneous and self-limiting reaction and the positive bias oxidizes the EGaIn electrode further, thereby forming a thicker oxide film.

2.2. Effect of the Conductivity and pH of the Electrolyte Solutions on the Rectification at the Interface of EGaIn/Electrolyte/Pt

The forward current of the device with EGaIn/electrolyte/Pt interface originates mostly from the electrolysis of water or electrolyte.

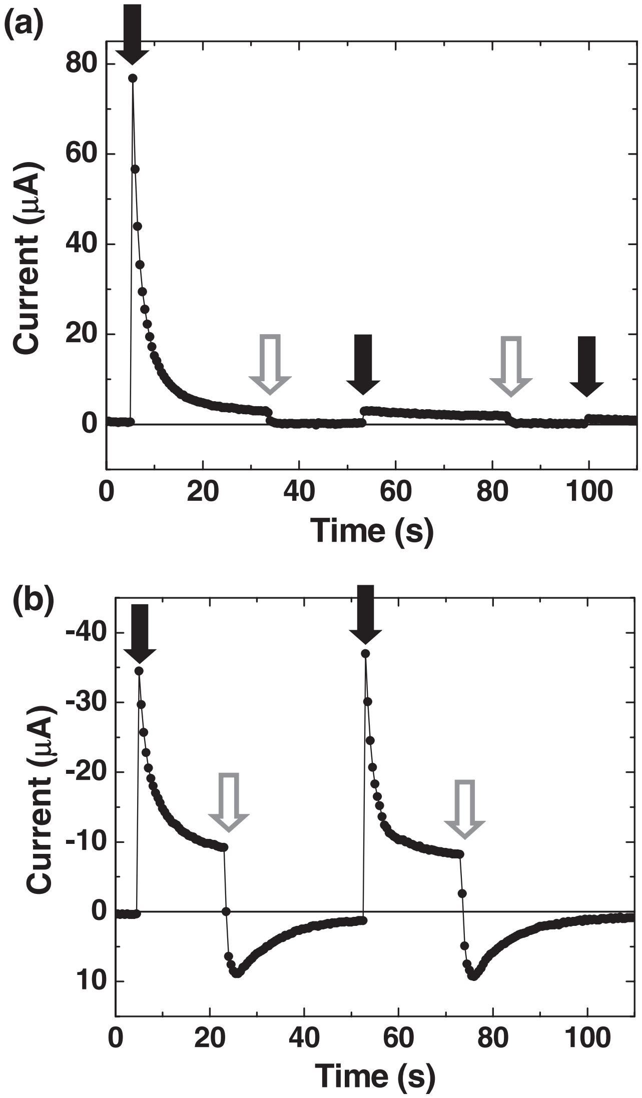

Figure 3. Current of an EGaIn/H_2O/Pt diode under repetitive oxidative (+3 V) (a) and reductive (–3 V) (b) biases with time. The filled and empty arrows indicate the time when the bias was turned on and off, respectively.

The rate of electrolysis should depend on the ionic conductivity of the electrolyte between the two electrodes. To investigate the effect of the conductivity of the electrolyte on the device performance, we prepared four different concentrations of sodium phosphate buffer solution with neutral pH. The conductivity of these electrolyte solutions varies from 0.093 mS cm^{-1} to 31 mS cm^{-1}, which is more than 300× higher than the lowest conductivity. The effect of the conductivity of the electrolyte on the forward/backward current of the device is shown in **Figure 4**. The forward current increases in proportion to the conductivity of the electrolyte, while the backward current is not affected as much as the forward current. The backward current is limited by the oxide layer rather than the conductivity of the electrolyte media. Due to the dominant dependence of the forward current on the electrolyte concentration, the rectification ratio of the device increases with the conductivity of the electrolyte (Figure 4c),

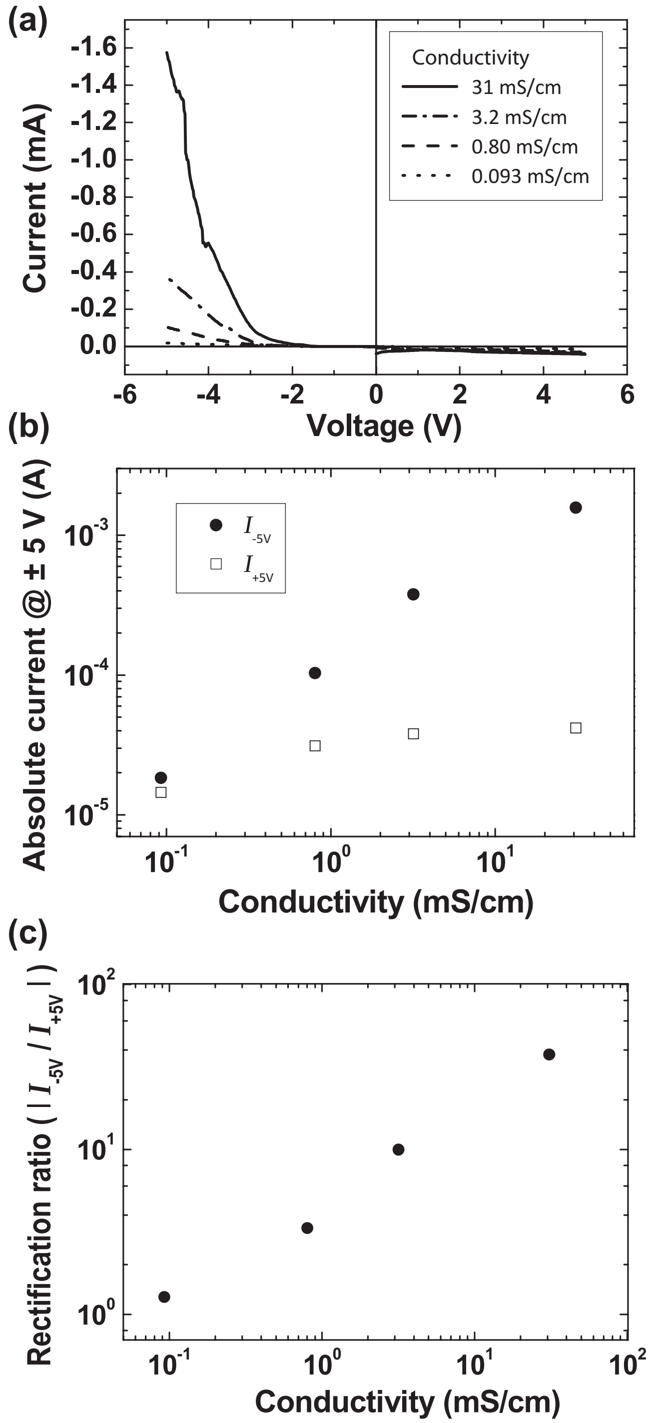

Figure 4. Effect of the conductivity of the electrolyte on the rectification behavior. a) Current as a function of applied voltage of the devices with different conductivity of the electrolyte. b) Current values and c) rectification ratios at ±5 V in terms of the conductivity of the electrolyte. The conductivity of the electrolyte varies by the phosphate buffer concentration. The rectification ratios were calculated from the current at ±5 V bias. The pH of the electrolyte buffer solutions is ~7.

which can be fitted with a power law dependence with an exponent ~0.6. This dependence reflects the complex difference in the device conductivity on the forward and the backward ion currents. Contrary to polyelectrolyte gel diodes that we reported previously (which rectify at the gel/gel interface),[4] the diodes based on oxide films, such as SNAGI diodes[5] and EGaIn/electrolyte/Pt diodes, show higher rectification performance at higher ionic conductivity, resulting from the efficient suppression of the backward current by the oxide barrier.

The pH of the electrolyte solutions could affect the rectification of the diodes since strong acids or bases etch the oxide layer.[40] The formation of the insulating oxide film during the positive sweep is a key mechanism for suppression of the backward current. We studied the effect of the electrolyte medium pH on the rectification by using solutions of polyacrylic acid (PAA), polyethylene imine (PEI) and sodium phosphate buffer (**Figure 5**). The pH values of the PAA, sodium phosphate buffer and PEI electrolyte solutions are ~3, ~7, and ~11, respectively. We adjusted the conductivity of the solutions to the same value (~810 μS cm^{-1}) by controlling the concentrations of the electrolytes to avoid the effects of conductivity, discussed earlier. The negative sweep of the I–V traces shows no significant dependence of the forward current on the pH of the electrolytes. The positive sweep, however, suppresses the current at pH 3 (PAA

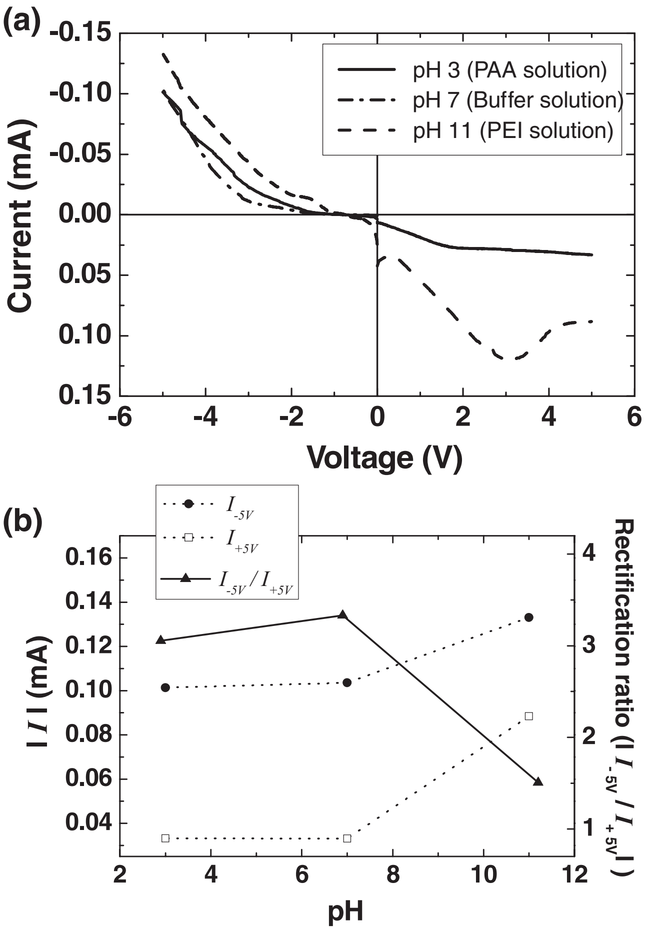

Figure 5. Effect of pH of the electrolyte interfacing the liquid-metal electrode on the rectification behavior. a) Current as a function of voltage of the device with electrolytes of different pH values. b) Current values at ±5 V bias and rectification ratios in terms of pH of the electrolytes. The conductivity of the electrolyte solutions are ~810 μS cm^{-1}.

solution) and 7 (neutral buffer solution), whereas large backward current is measured at pH 11 (PEI solution) resulting from the poor stability of the oxide film.[40] The current peak observed at ~3 V is likely associated with electrochemical events that only occur in the absence of the passivating skin. We observed a similarly shaped *I–V* trace in devices featuring a NaOH solution with the same pH as the PEI solution. The characteristic shape of the *I–V* trace at basic pH values may be explained by the competition of the oxidation reaction due to the bias and the removal of the oxide by base or, alternatively, the mass-transfer limited reaction typically shown in potential sweep methods.[41] Based on the current at ±5 V, the device showed the highest rectification ratio with the neutral pH electrolyte and the lowest rectification ratio with the basic pH electrolyte due to the inefficient suppression of the backward current (Figure 5b).

2.3. Ionic Current Rectification at the Interface of EGaIn/Hydrogel/Pt

The use of liquid electrolyte solution in the EGaIn/electrolyte solution/Pt diode could limit the usability of practical devices due to leakage of the liquid medium. Hydrogel infused with the electrolyte could replace the liquid medium for better encapsulation and ease of handling. Moreover, charged groups along the polymer backbone of the gel can improve the ionic conductivity,[5] thereby increasing the forward current and the rectification performance. The *I–V* trace of such a device with EGaIn/hydrogel/Pt interface is shown in **Figure 6**. The hydrogel contains 98 wt.% of the sodium phosphate buffer solution with a conductivity of ~31 mS cm^{-1} and 2 wt.% of agarose. Due to the increased ionic conductivity by the gel, the forward current at –5 V increased by a factor of ~3 compared to devices containing the same concentration of sodium phosphate buffer dissolved in water (solid line in Figure 4a). It should be noted that the backward current is also efficiently suppressed to ~0 μA in the device with the gel. The diode exhibits a rectification ratio as high as ~450 at ±5 V. Thus, replacing the electrolyte solution with hydrogel creates an ionic charge transport diode with improved rectification performance.

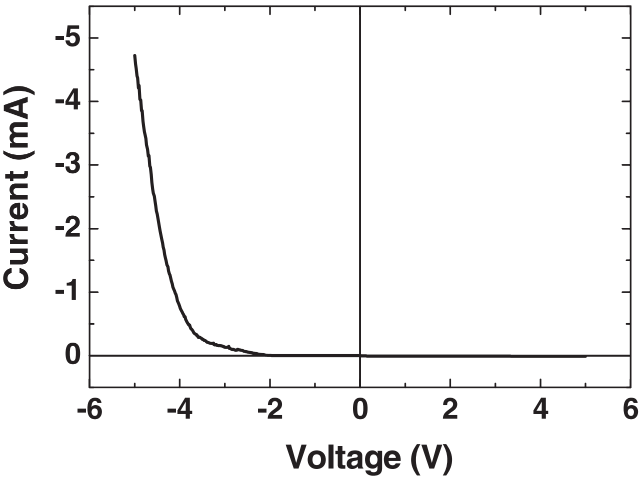

Figure 6. Representative *I–V* trace of a diode comprised of EGaIn/hydrogel/Pt. The hydrogel is made of an aqueous sodium phosphate buffer solution with a conductivity of 31 mS cm^{-1}.

2.4. All-Soft-Matter Diodes Formed Using Asymmetric Polyelectrolyte Gels with Different pH

The previously described devices have rigid Pt electrodes. To fabricate diodes composed entirely of flexible soft materials, we replaced the Pt electrode with a second EGaIn electrode and fabricated diodes comprised of EGaIn/hydrogel 1/hydrogel 2/EGaIn. Asymmetry is required for diode rectification. In the diodes containing Pt, the asymmetry arises from the fact that EGaIn can form an insulating oxide skin but Pt does not. To achieve asymmetry in the EGaIn/hydrogel 1/hydrogel 2/EGaIn structure, we stacked two gel layers each doped with different polyelectrolytes to control the local pH values as shown in **Figure 7**a. The *I–V* trace in Figure 7b demonstrates that the current increases with negative bias and suppresses in the positive bias to achieve a rectification ratio of ~14. We investigated the transient response of the soft-matter device under alternating electric field with a frequency of 0.5 Hz (Figure 7c). We connected the diode in series with a 100 kΩ resistor and measured the voltage differential across the electrodes, which is proportional to the diode resistance. The graph clearly shows rectification due to asymmetric conductance. In the high-resistance state (high output voltage periods), the voltage gradually increases with time, possibly because of the delayed charging process limited by the diffusion of ions after sudden change of the voltage.

The structure and the operating mechanism of these all-soft-matter-based diodes are shown in Figure 7d. Two EGaIn electrodes sandwich the two gel layers doped with PAA and PEI (i.e., EGaIn/PEI gel/PAA gel/EGaIn). In the absence of electric bias, the PEI polyelectrolyte gel is basic enough to remove the oxide skin on the EGaIn electrode, and thus, the oxide film forms only at the interface between the PAA polyelectrolyte gel and the EGaIn electrode. Applying a positive bias (backward bias) to the EGaIn/PAA gel leads to formation of a thick oxide film at the interface of EGaIn/PAA and suppresses the current through the device. However, applying a negative bias (forward bias) to the EGaIn/PAA gel reduces the oxide skin at the interface of EGaIn/PAA and renders the diode conductive since the interface of the EGaIn/PEI electrode remains relatively free of oxide due to the local pH. Rectification behavior is not observed in devices featuring two Pt electrodes (Figure S3), which confirms that the asymmetric interfaces of the polyelectrolyte gel/EGaIn electrodes (EGaIn/PAA gel and EGaIn/PEI gel) rather than the junction of the two polyelectrolyte gels (PEI gel/PAA gel) play an important role in the diode characteristic of the all soft-matter device. The same configuration can achieve memristor-like behavior (i.e., resistive switching) depending on the history of the applied bias, which has been reported elsewhere.[21] Thus, we demonstrate a prototype diode composed entirely of soft matter based on interfacing EGaIn electrodes with hydrogels doped with different polyelectrolytes. Under alternating electric field with high frequency, the slow ion mobility could be a limitation in such devices operated by ionic

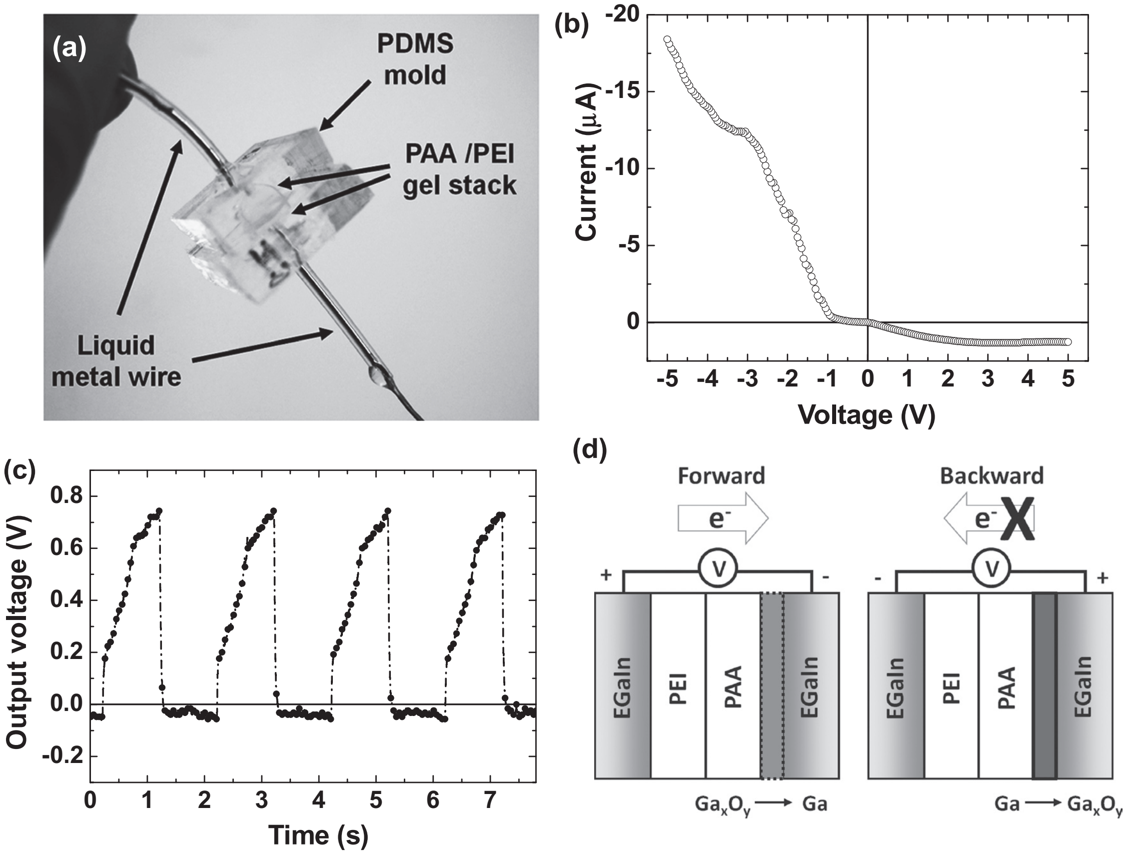

Figure 7. a) Photograph of a prototype diode composed entirely of soft matter. b) Current as a function of applied voltage and c) Transient voltage response under AC signal of the soft-matter diode. The EGaIn electrode interfacing the PEI gel is grounded. The output voltage is the voltage applied to the diode under AC bias with amplitude of ±3 V. d) A schematic depiction of the soft-matter diode with asymmetrically configured polyelectrolyte gels under forward and backward biases.

current.[5] Scaling down of the device dimensions can allow the operation of the device at faster bias change rates. Further experiments are under way to establish the effect of the device dimensions on the operation frequency range of these diodes.

3. Conclusions

We demonstrate ionic current rectification in a system composed of EGaIn liquid-metal/electrolyte-solution/Pt. Rectification is achieved by the formation and reduction of the insulating oxide film on the EGaIn electrode. The asymmetric configuration of the electrodes (i.e., electrochemically active EGaIn and inert Pt) enables the current to flow unidirectionally. The forward current is limited by ion transport and depends on the conductivity of the electrolyte solution. The backward current is suppressed by the formation of the oxide film on the EGaIn and is affected by the pH of the electrolyte solution, which changes the stability of the oxide layer on EGaIn. Replacing the electrolyte solution with hydrogel provides better encapsulation of the electrolyte solution and improves rectification performance as high as ~450 by increasing the conductivity. Finally, we constructed prototypes of diodes composed entirely of soft matter by interfacing EGaIn electrodes and polyelectrolyte gels with different local pH. The materials used in these devices are flexible, moldable, and soft, and their fabrication process is simple. As the soft-matter diodes operate based on ionic current and reactions of EGaIn electrodes with aqueous electrolytes, they are compatible with water-based or high humidity systems. Since biological systems generally have soft, curved, and in some cases moving surfaces and tend to be operated by ionic current rather than electronic current, such a soft, ionic current diode could find potential applications in neuromorphic systems, bio-embeddable smart particles and biomimetic devices.

4. Experimental Section

The EGaIn electrodes in the device comprised of EGaIn/electrolyte/Pt, were prepared by injecting the liquid metal into a linear microfluidic channel. EGaIn protruding out of one end of the channel was interfacing electrolyte solutions or hydrogels. The stock phosphate buffer solution was made by mixing 0.2 M NaH_2PO_4 and 0.2 M Na_2HPO_4 aqueous solutions at a ratio of 4:6. The conductivity of the electrolyte solutions was varied by changing the concentration of the stock buffer solution. To investigate the effect of pH environment on the rectification performance of the diode, the PAA (M_w 100 000, Sigma–Aldrich) and PEI (M_w 750 000, Sigma–Aldrich) polyelectrolytes were added to water until the conductivity becomes comparable with that of the reference buffer solution with neutral pH (~810 µS cm^{-1}).

The hydrogel was prepared by following the procedure reported previously.[5] The stock phosphate buffer solution was used to prepare the gel with high conductivity. PAA (7.2 wt.%) and PEI (5.7 wt.%) were added as dopants of polyelectrolyte gels to form the asymmetric junction of all soft-matter-based diodes. The detailed fabrication procedure of the device is described in our previous report.[21]

The *I–V* characteristic curves were obtained by using a computer controlled source meter (Keithley 2400, Keithley Instruments Inc.). The time dependent current behavior under repetitive and continuous biases was measured by using DC regulated power supply (Extech Instruments) and a digital multimeter. The transient responses of the prototype of all soft-matter diodes to AC bias were measured using a function generator and computer-controlled digital oscilloscope (22120A, 34405A, and DSO3202A, respectively, all products of Agilent Technologies). A square-wave AC signal with a frequency of 0.5 Hz and amplitude of ±3 V was applied to the device connected in a series with a 100 kΩ resistor when measuring the AC voltage across the device.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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