Ionic current devices—Recent progress in the merging of electronic, microfluidic, and biomimetic structures

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We review the recent progress in the emerging area of devices and circuits operating on the basis of ionic currents. These devices operate at the intersection of electrochemistry, electronics, and microfluidics, and their potential applications are inspired by essential biological processes such as neural transmission. Ionic current rectification has been demonstrated in diode-like devices containing electrolyte solutions, hydrogel, or hydrated nanofilms. More complex functions have been realized in ionic current based transistors, solar cells, and switching memory devices. Microfluidic channels and networks—an intrinsic component of the ionic devices—could play the role of wires and circuits in conventional electronics. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4804249>]

I. INTRODUCTION

The ubiquitous electronic devices that make modern life possible predominantly operate by electron transport through metallic or semiconducting circuit components. Even these devices, however, include a few components, notably batteries and electrolytic capacitors, which rely on ionic charge generation and transport. The situation is drastically different in the biological domain, where many processes, ranging from photosynthesis to the functioning of the neurons and the brain, involve ionic migration and ionic currents. Ionic currents on the microscale and nanoscale can underlie the operation of future generations of man-made devices, which can interface and be intrinsically compatible with biological tissues. The micro- or nanoscale confinement of the liquid or semi-liquid medium, in which the ion transport takes place, naturally brings these devices into the microfluidic domain. We provide here a review and perspective on the recent developments of such ionic current devices.

The operation of the ionic current devices is dependent on the ion transport near charged surfaces in water medium. Due to the overall charge neutrality and local electrostatic attraction, each charged surface in water medium is surrounded by a highly concentrated layer of mobile counter-ions. The role of the mobile ions as a current carrier becomes more pronounced when the counter-ionic layers overlap in nanoscale proximity. One of the most intriguing ways to modulate the ionic current is to confine the electrostatic interactions with wall surface charges to the nanoscale.^{1,2} The electric potential away from the charged surface, Ψ , decays approximately exponentially as described by the equation, $\Psi(x) \approx \Psi_s \exp(-\frac{x}{1/\kappa})$, where Ψ_s is the potential difference between the surface and the bulk, x is the distance away from the surface, and $1/\kappa$ is the characteristic decay distance known as the Debye length.³ Since the Debye length of aqueous solutions is usually less than 100 nm, nanofluidic channels with charged walls could control ionic flows through the surface charge of the channel walls.⁴ Charged nanochannels with diameter smaller than the Debye length enable selective transport of only one type of ions by electrostatic gating. Instead of confinement, the ionic current can be controlled by system asymmetry.

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Interfacing of two electrolyte or polyelectrolyte media, with ionic carriers of opposite charge, allows rectification and making of nonlinear devices, broadly analogous to the opposite electronic carriers in p or n type semiconductors. Nonlinear conductivity and redox reaction of insulating oxide films can also control the directional ionic flow. The means used to control ionic currents with examples from literature sources are summarized in Table I.

Due to their ability to operate in aqueous phase, ionic current devices could find a range of bio-related applications, such as sensing, separation and manipulation of biomolecules. Nonlinear ionic current are also generated in a number of essential processes in the human body. For example, adenosine triphosphate (ATP), the energy source in the body, can be synthesized by selective transport of protons through a biological channel called ATP synthase. A neural signal is transmitted by propagation of action potential induced by preferential diffusion of Na^+ ions through the neural membrane.

In this perspective, we first review the results on rectification of ionic currents, corresponding to the function of the basic electronic diodes. We then discuss the emergence of more complicated functions by modulating ionic current in recent studies of ionic transistors, memristors, and solar cells. Sections IV and V focus on a discussion how microfluidics can be used as

TABLE I. Representative means of controlling ionic currents and the corresponding phenomena and applications.

Means	Schematics	Phenomena/applications
1. Electric field		Electrophoresis, electric double layer on charged surfaces
2. Geometry of ion-channels		Selective ion transport due to overlapping of electrical double layers Rectification by selective ion transport
3. Immobilization of ions		Using the two types of oppositely charged mobile ions as local charge carriers, analogous to electrons/holes in semiconductors
4. Electro-chemical reactions		Formation or removal of ion-depletion layer or non-conducting film (e.g., oxide)

means of fabricating the host matrix and wiring the ionic devices into early prototypes of electric and biomimetic circuits.

II. IONIC DIODES

A diode is a basic electronic component exhibiting current rectification by readily conducting electric current in one direction and inhibiting the reverse current. The making of rectifying ionic devices has been achieved by numerous means, which are exemplified schematically in Figure 1 and reviewed below.

FIG. 1. Examples of ionic current rectifying systems. (a) Ionic current rectification in a nanochannel with asymmetric charge distribution. Reproduced with permission from Daiguji *et al.*, Nano Lett. **5**, 2274 (2005). Copyright 2005 ACS Publications. (b) A cone-shaped nanotube with asymmetric charge distribution. Reproduced with permission from Vlasiouk and Siwy, Nano Lett. **7**, 552 (2007). Copyright 2007 ACS Publications. (c) A polyelectrolyte diode with oppositely charged counter ion carriers. Reproduced with permission from Cayre *et al.*, J. Am. Chem. Soc. **129**, 10801 (2007). Copyright 2007 ACS publications. (d) A polyelectrolyte diode on a microchip. Reproduced with permission from Han *et al.*, Angew. Chem., Int. Ed. **48**, 3830 (2009). Copyright 2009 John Wiley & Sons, Ltd. (e) Selective ion transport in a device with the interface of hydrogel/SiO₂ nanofilm. Reproduced with permission from Koo *et al.*, Small **6**, 1393 (2010). Copyright 2010 John Wiley & Sons, Ltd. (f) Ionic current rectification in an entirely soft device composed of hydrogels and liquid metal. Reproduced with permission from So *et al.*, Adv. Funct. Mater. **22**, 625 (2012). Copyright 2012 John Wiley & Sons, Ltd.

An asymmetric distribution of the surface charge on the nanochannel walls could allow ionic current rectification. Daiguji *et al.* theoretically proved that a nanofluidic diode can be realized when the surface of either half of the channel is oppositely charged as shown in Figure 1(a).⁵ Karnik *et al.* demonstrated nanofluidic diodes with asymmetric charge distribution by modifying one half of the neutral surface of biotin-adsorbed channel with positively charged avidin.⁶ Gracheva *et al.* proposed a design of an electrically tunable rectifying membrane consisting of p-n semiconductor layers.⁷

The use of asymmetrically shaped nanochannels with charged walls also enables ionic current rectification. Siwy and coworkers performed both theoretical and experimental studies on selectivity and rectification of ionic current in cone-shaped nanochannels (Figure 1(b)).^{1,8–10} Extensive study on inversion of the ionic current rectification depending on the surface charge density of the cone-shaped channels was conducted by Yu *et al.*¹¹ Cone-shaped nanopores with grafted DNA layers have been proposed as artificial ion channels where ionic current is rectified via electromechanical action of the bio-polyanions.¹² The negatively charged, flexible, DNA chains attached on the asymmetric nanopores move into and out of the small opening depending on the bias polarity, thereby gating the ionic current. Yossifon *et al.* reported a nonlinear ion flux resulting from instability of space-charge layer at only one of the asymmetric entrances of nanoslot arrays.^{13,14} A pH-tunable nanofluidic diode with a cone-shaped amphoteric nanopore has also been constructed.¹⁵ Similarly, ionic current rectification has been measured in nanopipettes with tapered openings.^{16,17} Such nanochannel based devices could provide a precise control of small volume of an ionic flow with well-defined nanostructures. The ionic current flows in a nanoscale can be conveniently interpreted by electrokinetic phenomena in a laminar regime. The magnitude of the current in these devices lies in the nanoampere range, which could be a hurdle to interfacing conventional systems, but may open applications in ultralow current devices.

On a large scale, the formation of an ion depletion region at an interface of electrolytes was used for ionic current rectification. Intensive research on the ionic current rectification at a junction of acidic and basic electrolytes has been conducted.^{22–26} The rectifying junction of these electrolyte diodes is formed in the hydrogel bridge which connects two electrolyte reservoirs. During reverse bias, where positive potential is applied to the electrode in the acid solution, H^+ and OH^- ions migrating from the electrolytes form water at the interface, where the ion concentration is drastically reduced. This junction has high impedance and acts as a depletion layer in a p-n junction diode. The formation of a more practical and stable device with nonlinear current response at the interface of two polyelectrolyte hydrogel layers was reported by Cayre *et al.* Figure 1(c).¹⁸ The device is formed by interfacing two hydrogel layers doped with oppositely charged polyelectrolytes. The charged mobile counterions from the gels act as oppositely charged carriers and form a rectifying junction at the interface. The hydrogel matrix provides an excellent conductive medium for stable encapsulation of the liquid solution and polyelectrolytes. Conroy *et al.* performed in-depth theoretical and experimental research on a hysteretic current response under reverse bias in a bipolar hydrogel membrane.²⁷ Han *et al.* demonstrated a prototype logic circuit device by integrating similar polyelectrolyte diodes on a microchip Figure 1(d).¹⁹

Ionic current diodes can also be constructed on the basis of a the nonlinear electrical conductivity of hydrated SiO_2 layer between electrolyte and Si substrate.²⁸ We have demonstrated a highly efficient ionic current diode formed by bringing the SiO_2 nanolayer into contact with agarose gel Figure 1(e).²⁰ Optimum agarose concentration of 0.5 wt. % and doping with negatively charged polyelectrolyte and salt increases the ionic conductivity of the hydrogel, drastically improving the rectification performance. We also presented an ionic current diode composed entirely of soft matter: hydrogels, and liquid metal Figure 1(f).²¹ Two polyelectrolyte hydrogel layers provide different pH environment on liquid metal (eutectic gallium indium, EGaIn) electrode surfaces, affecting the stability of the insulating oxide skin on the liquid metal. One liquid metal electrode interfacing a hydrogel layer with embedded polyethyleneimine (PEI) forms oxide-free surface due to high pH medium and is always conductive regardless of bias polarity. The thickness of the oxide layer at the other interface between the

hydrogel with embedded poly(acrylic acid) (PAA) and the EGaIn changes depending on bias polarity, where the forward bias leads to oxide reduction and high charge transport. Thus, different formation and dissolution rates of the oxide skin at each hydrogel/liquid metal interface under electric bias enable ionic current rectification.

The rectification ratio, obtained by dividing the forward current direction by the reverse current, is one of the important parameters to evaluate a diode performance. The rectification ratios of ionic current diodes reported in the literature are summarized in Table II. The rectification ratios of the ionic current devices are generally low and not comparable with the conventional inorganic diode operated by electronic current. The low ratios possibly result from inefficient suppression of backward ionic current. For example, Vlassiuk and Siwy¹⁰ and Cheng and Guo³⁰ reported relatively high rectification ratios of 217 and 321 with 2–20 nm channel diameter, which is more than one order of magnitude smaller than dimensions of other channels. Smaller channel diameter enhances the selectivity of ions by electrostatic interaction from the charged inner surface of the channels. Our device with SiO₂/hydrogel interface achieved extremely high rectification ratio of 38 000,²⁰ possibly as a result of the highly proton-selective current in the insulating oxide film that efficiently blocks the ionic current during reverse biasing.

III. IONIC TRANSISTORS, MEMRISTORS, AND SOLAR CELLS

The recent developments of more complex means of ionic current control enabled the construction of more sophisticated devices. Karnik *et al.* and Fan *et al.* reported an ionic current transistor with silica nanochannels on which gate electrodes were placed (Figure 2(a)).^{33,34} The voltage applied to the gate controls the proton ion concentration in the silica channels, thereby modulating the ion conductivity through the channels, similar to the operation mechanism of field-effect transistors (FETs). Kalman *et al.* demonstrated ionic current bipolar junction transistors (BJTs) with double-conical nanopore, where the pore wall was separated by three different charge regions (positive-negative-positive).³⁵ The on/off switching of ionic current was performed chemically by changing the pH and concentration of electrolyte. Theoretical study of ion transport in nanofluidic devices also proved that an ionic current flow in nanofluidic channels with three different charged regions on the wall can be modulated depending on the charge density on the “gate” wall.⁵

Intense research has been conducted on photoelectrochemical cells with liquid medium,³⁶ where ionic current in electrolyte solution is involved in the regeneration processes of light-harvesting molecules. We reported recently an alternative design of a water-based photovoltaic system using gel matrices photogenerating an ionic current (Figure 2(b)).³⁷ Two photoactive dye ions embedded in a hydrogel matrix generate electrical current when photoexcited. A provisional

TABLE II. Comparison of the rectification ratios of ionic current diodes reported in the literature.

Rectification principles	Underlying mechanisms from Table I	Authors and publication year	Rectification ratios (sweep bias)
Acid-base electrolyte junctions	1, 4	Hegedüs <i>et al.</i> 1999 ²³	~40 (± 5 V)
Conical nanochannels with asymmetrically charged inner walls	1, 2	Vlassiuk <i>et al.</i> 2007 ¹⁰	217 (± 5 V)
Polyelectrolyte junction with oppositely charged backbones	1, 3, 4	Cayre <i>et al.</i> 2007 ¹⁸	~40 (± 5 V)
Conical nanochannels with charged polymer brushes	1, 2	Yameen <i>et al.</i> 2009 ²⁹	22 (± 2 V)
Nanochannels with asymmetrically charged inner walls	1, 2	Cheng <i>et al.</i> 2009 ³⁰	321 (± 1 V)
Nanochannels with asymmetric geometries and concentration polarization	1, 2	Jung <i>et al.</i> 2009 ³¹	~2 (± 3 V)
Polyelectrolyte junctions with oppositely charged backbones	1, 3, 4	Han <i>et al.</i> 2009 ¹⁹	~100 (± 1 V)
Nanochannels with asymmetrically charged inner walls	1, 2	Yan <i>et al.</i> 2009 ³²	~5 (± 5 V)
Nonlinear conductivity of a SiO ₂ nanofilm/agarose gel interface	1, 2, 3	Koo <i>et al.</i> 2010 ²⁰	38 000 (± 5 V)
Electric bias- and pH-dependent formation of insulating oxide layer	1, 4	So <i>et al.</i> 2012 ²¹	~14 (± 5 V)

FIG. 2. Examples of ionic current devices with more complex functionalities. (a) A nanofluidic transistor. Reproduced with permission from Karnik *et al.*, *Nano Lett.* **5**, 943 (2005). Copyright 2005 ACS Publications. (b) A hydrogel based photovoltaic cell. Reproduced with permission from Koo *et al.*, *J. Mater. Chem.* **21**, 72 (2011). Copyright 2011 the RSC. (c) A soft memristor composed of hydrogels and liquid metal. The graph at the bottom illustrates the resistive switching characteristic of the device. Reproduced with permission from Koo *et al.*, *Adv. Mater.* **23**, 3559 (2011). Copyright 2011 John Wiley & Sons, Ltd.

mechanism of the device operation based on a synergistic effect of the two dye ions and ionic characteristic of photocurrent suggested that two dye ions work cooperatively in the gel, by facilitating electron transport and regenerating oxidized dye molecules. A flexible prototype of a photovoltaic device was constructed on the basis of the soft hydrogel matrix and plastic film conducting electrodes. Biologically derived molecules, such as Chlorophyll and Photosystem II, could be used as photoactive components in the aqueous gel media of such devices.

Another class of nonlinear elements that our group demonstrated recently is quasi-liquid resistive switching memory devices composed of hydrogels and liquid metal (Figure 2(c)).³⁸ Asymmetric pH environments provided by two polyelectrolyte gel layers caused different formation rates of the oxide skin on two liquid metal electrodes. The device has two discrete states of ion conductivity, depending on the polarity of the pre-bias voltage. Formation and reduction of the insulating oxide skin by electric bias determined the resistance state of the whole stack. The switchable formation of a permanent oxide skin enabled the device to exhibit memristive characteristics. Such devices composed of soft biomimetic matter could find applications in future neuromorphic systems.

IV. MICROFLUIDICS OUTLOOK—FUNCTIONAL MICROFLUIDIC MATERIALS

The ionic devices are generally made of liquid and hydrated soft matter, which are commonly hosted in microfluidic networks. To place this intrinsic relation in perspective, we overview briefly the recent research on functional materials with microfluidic networks, first from a general perspective, and then as promising structures for ionic device integration. Soft materials with embedded microvascular networks can serve as a flexible and reconfigurable matrix for constructing 2-D or 3-D architectures with fluidic or electronic functionality. Depending on the physical, chemical, and electrical properties of the fluid in the channels, the resulting

microvascular materials can achieve a wide variety of functionalities, a few of which are illustrated in Figure 3.

Chang *et al.* reported a shape-memory elastomer with microvascular networks (Figure 3(a)).³⁹ When the liquid photocurable polymer in the channels is solidified by UV illumination, it retains the user-defined shapes. Siegel *et al.* reported a technique called microsolidics by injecting liquid solder into microfluidic channels and solidifying by cooling.⁴⁰ The technique has offered a facile way to construct a complex metallic structures. So *et al.*⁴¹ and Kubo *et al.*⁴² described a technique for fabricating a flexible and stretchable microfluidic antenna, where the channels were filled with a highly conductive liquid metal alloy (Figure 3(b)). A simple stretchable radio frequency electronic device was also demonstrated with a liquid alloy-filled microfluidic antenna.⁴³ Toohey *et al.* reported a 3-D microvascular network-embedded material with a self-healing function, inspired by the blood vessels protecting human skin (Figure 3(c)).⁴⁴ The microvascular channels rapidly and efficiently supplied a liquid healing agent, which enabled repetitive healing of the cracked surface of the materials. Transparent soft elastomers with microfluidic channels can be used as smart windows or robot-camouflage materials, changing their color, contrast, or luminescence depending on filling solution

FIG. 3. Examples of functional microfluidic materials. (a) Soft materials of controlled shape and stiffness. Microvascular networks filled with a photocurable polymer allow retaining a pre-defined shape after UV illumination. Reproduced with permission from Chang *et al.*, *Adv. Mater.* **21**, 2803 (2009). Copyright 2009 John Wiley & Sons, Ltd. (b) Reversibly deformable microfluidic antenna filled with conducting liquid alloy. Reproduced with permission from So *et al.*, *Adv. Funct. Mater.* **19**, 3632 (2009). Copyright 2009 John Wiley & Sons, Ltd. (c) Schematic and optical image of a self-healing microfluidic material filled with a polymerizable healing agent. The healed cracks are visible in the image. Reproduced with permission from Toohey *et al.*, *Nature Mater.* **6**, 581 (2007). Copyright 2007 Nature Publishing Group. (d) Color changing soft materials with microfluidic networks. (Top) A microfluidic elastomer sheet demonstrating a color change from red to blue. Reproduced with permission from Uçar and Velev, *Soft Matter* **8**, 11232 (2012). Copyright 2012 the RSC. (Bottom) A soft robot with microfluidic channels filled with chemiluminescent solution. Reproduced with permission from Morin *et al.*, *Science* **337**, 828 (2012). Copyright 2007 AAAS.

(Figure 3(d)).^{45,46} As opposed to microfluidic devices made of conventional materials, highly porous gel-based microfluidic devices could utilize the mass transport through the channel walls for efficient supply or exchange of solute molecules. Stroock and coworkers reported microfluidic scaffolds based on alginate hydrogel for tissue engineering.^{47,48} They have investigated the convective and diffusive transport mechanisms in microfluidic hydrogel matrices with various channel structures as means to control the distribution and supply of solutes in a bio-scaffold.

V. MICROFLUIDIC STRATEGIES FOR DESIGN OF IMPROVED IONIC CURRENT DEVICES

Compared to normal electronic devices, the ionic current based devices have the potential to be more readily interfaced with biosystems where the ionic current is the dominant signal carrier. Since ions are intrinsically slower than electrons, however, the operational speed of the ionic current based devices could be an obstacle to practical applications. One can compensate for the disadvantage of the ionic system by miniaturizing the conductive paths or operating parallel circuits. 2D- or 3D-microfluidic networks could provide a feasible template for wiring the ionic device component. Microfluidic channels can also serve as a means for efficient supply and replenishment of active ions, which allows repeated regeneration of ionic devices.

Materials with microfluidic networks similar to the ones mentioned in Sec. IV represent a promising platform for parallel device integration. Recently, a series of wiring techniques and integrated circuits based on microfluidic channels have been demonstrated. The channels can be simply filled with a highly conducting fluid, such as liquid metal.⁴⁹ We demonstrated how a small array of hydrogel memristors can be integrated in the first prototype of an ionic current based memory circuit, by wiring them through channels filled with liquid EGaIn (Figure 4(a)).³⁸ The microchannel design of this multiple-element device has crossbar array structure, where each intersection is a single memristive node.

The fluidic or gel environment in ionic current devices allows for the ions participating in device operation to be replenished and replaced,⁵⁰ a regeneration capability that can hardly be achieved in conventional electronics composed of stationary solid phase materials. This enables

FIG. 4. Ionic current devices hosted by microfluidic networks. (a) Integration of memristor elements in a soft matrix by using microfluidic channels. Each intersection of the crossbar array channels acts as one memory node, as shown in the bottom image. Reproduced with permission from Koo *et al.*, Adv. Mater. **23**, 3559 (2011). Copyright 2011 John Wiley & Sons, Ltd. (b) A schematic of a new photovoltaic concept with biomimetic regeneration functionality.⁵¹ The embedded microfluidic network allows uniform and efficient replacement of photoactive molecules or electrolyte ions.

the repeated regeneration of ionic current devices after photodegradation or electrochemical damage of active ionic species. Microfluidic networks offer the means for efficient supply or replenishment of the active molecules similar to the continuous operation of the photosystems in a natural leaf. The concept of a microfluidic hydrogel solar cell with biomimetic regeneration functionality is schematically shown in Figure 4(b).⁵¹ Photovoltaic reagents, dyes, and redox electrolytes can be uniformly delivered via microfluidic networks embedded in porous media, such as a hydrogel.^{47,48,52,53} Such photovoltaic cells with embedded microfluidic networks show the way to biomimetic regenerative ionic-microfluidic devices.

VI. CONCLUDING REMARKS

Ionic current devices are emerging as a potential bridge between artificial and biological circuit and sensing systems. Intensive research has led to various means of ionic current rectification by using charged nanostructures, forming ion depletion barriers, and manipulating insulating oxide layers. Ionic current devices with functionalities beyond basic rectification, such as transistors, photovoltaic cells, and memristors are presently emerging as the next research frontier. As the operation speeds of the ionic devices are much slower than that of the electronic ones, it is likely that the ionic electronics will first penetrate areas that are unfeasible for conventional electronics—such as devices that interface liquid medium, biological systems, and live organisms. Microfluidic networks could serve as a platform for this forthcoming multi-level environmental and biological integration. Moreover, the use of microfluidic channels can enable an additional biomimetic functionality that complements the electrical ionic transport, such as mechanical actuation, sensing, and self-regeneration.^{50,51,54–58} As an example, the functionality imitating the regeneration procedure of photoactive biomolecules in a natural leaf can be realized on the basis of dynamic replacement of active ions via the microfluidic networks in ionic devices. Thus, the combination of microfluidics with ionic electronics could in the future lead to exciting new generations of biomimetic/electronic devices.

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