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# Differentiated Ionic Electroresponse of Asymmetric Bio-Hydrogels with Unremitting Power Output

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Cytomembranes with efficient ionic selectivity and energy circulation, essential for biological activities in multicellular organisms, are a source of inspiration for man-made biomedical devices. However, current man-made soft systems mainly imitate simple and passive cytomembranes behaviors, restrained by the grand challenge that lies at the meeting point of synchronous engineering of both (dynamic) ionic selectivity and (passive) transcellular-like potential in one structure. Here a dynamically differentiated ionic electroresponse and passive incessant power output of an asymmetric bio-hydrogel constructed using a simple self-propagative flow approach are reported. The unprecedented freely formed p and n analogue hydrogels yield a transcellular-like potential (110-200 mV) in response to diverse stimuliwhere the cathode or anode is capable of perceivable electroresponse to water and/or salt media, respectively. A single hydrogel can generate an output power density of 135-190 mW m<sup>-2</sup> superior to most bio-inspired soft and/or green power sources. The scalable manufacturing and proof-ofconcept demonstration elucidate the feasibility of mobilizing passive and dynamic behaviors in one structure. This work has the potential for realizing high-performance soft power sources in parallel to electrostimulation for neural excitation/inhibition, extending into the previously inaccessible region of biomedical applications.

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# 1. Introduction

The bioelectric signal is fundamental and significant to biological activity and evolution, emerging from multiple levels, the cell survival and propagation,<sup>[1-4]</sup> signal transmission in the nerve,<sup>[5-7]</sup> as well as the predation of animals,<sup>[8,9]</sup> for instance. For most bioelectric signals demonstrated so far, the external stimuli trigger the bio-voltage or current spikes, responding to the surroundings or transferring the information to the next acceptor.<sup>[10]</sup> The cytomembrane in living cells, typically, is excited by the ions and/or osmotic pressure on account of a number of channel proteins.<sup>[11-14]</sup> These channel proteins discern and regulate the ions through the cytomembrane-driven transcellular potential, accomplishing a dynamic ionic selectivity (Figure 1a[i]). Particularly, the water channel protein called aquaporin and electrogenic Na<sup>+</sup>–K<sup>+</sup> pump (Figure 1a[ii]), recognize and direct respective water molecules and inorganic ions with controlled spatial and flux concentrations, essential for many cell functions.[15] Simi-

larly in biology, the electric eels perfectly deploy the above features in their evolution, in which the arrangement of thousands of ion gradients enables electric discharges of 100 watts (W) for incapacitating prey.<sup>[16]</sup>

Hence, artificially engineered systems that can mimic some of these biological features are not only theoretically fascinating but also promises exciting opportunities for creating new type of material systems and autonomous devices. Inspired by the electric eels, artificial soft power sources mimicking the anatomy of electric eels had been demonstrated using the K<sup>+</sup> and Na<sup>+</sup> hydrogels, generating potential in excess of 100 V for several hours.<sup>[9]</sup> Another of such artificial system representation that, analogously, mimics the proton movement across the membrane is the moist-electric generator (MEG),<sup>[16-24]</sup> where the released protons induced by adsorbed water molecules exemplify yet a variant of contemporary soft power sources. However, this otherwise promising MEG discontinuously delivers electric output as the process of water adsorption attains an equilibrium state, presenting its shortcomings of sporadic power generation. Besides, some MEGs face materials integrity issues such as polymer dissolution under high moisture imbibement scenario while others are constrained in operating





**Figure 1.** Morphology and ionic selectivity in cytomembrane and asymmetric polyelectrolyte hydrogel. a) (i) Ionic selectivity in a variety of channel proteins of the cytomembrane containing sodium ion and potassium ion channel proteins (collectively known as  $Na^+-K^+$  pump), as well as water channel proteins, aquaporin (AQP). (ii) Ions are recognized by the specific channel proteins, yielding the transcellular potential. (iii) Differentiated ionic electroresponse in polyelectrolyte hydrogels resulting from the inverse ends. Biomaterials, that is, chitosan and sodium alginate, are used as polycation and polyanion, respectively. b) Formation of the polyelectrolyte hydrogel where the low-viscosity chitosan colloid self-propagates into the high-viscosity sodium alginate solution to form an asymmetric polyelectrolyte hydrogel.

conditions and structural architecture. Moreover, both dynamic and passive behaviors, mirroring biological behavior with potential in biomedical applications,<sup>[25]</sup> are hardly integrated into these generators. To take the nature-inspired soft devices to the next level, hybrid dynamic ionic electroresponse and passive unremitting power output should be devised holistically, capitalizing on the materials principle of upcycling biowaste for the circular economy. In addition, the current trends in designing power sources mainly by embedding ever more external energy input and routinely introducing complex nonrenewable multi-material constructs, have in fact reduced the opportunities for green, spontaneous, differentiated integration seen in the organism. To our knowledge, little headway to date has been made in the autonomous and synchronous manipulation of biomimetic device that entails both the dynamic and passive wealth of behaviors similar to the cytomembrane in media and signal transportation spatiotemporally. The tunable positive and/or negative voltage response may achieve selective neural excitation or inhibition, unequivocally advantageous to biomedical application.<sup>[25]</sup>

Herein we demonstrate a minimalist concept of selfpropagative flow approach in designing an asymmetric hydrogel, capable of orchestrating dynamically differentiated ionic electroresponse to passively output continuous energy (Figure 1a[iii]). Not rigid in conformation, the diffusive nature of the colloid is particularly befitting in providing a versatile and subtle approach to forming ion-selective graded structures. The fluidic nature, structurally dynamic, and regulable cation and anion constituents lead to the formation of pervasive p and n analogues within the polymeric networks in conjunction with the adaptability to any conformal geometry. This work highlights the upcycling of biomass into functional bionic hydrogels that 1) readily render free-form manufacturing via self-propagating colloid diffusion and coacervation reaction, 2) autonomously generate a continuous transcellular-like potential between their cathode and anode under low-power external stimuli, 3) manifest high stability in ambient and salt media, and 4) elicit sustainable excitation voltage, in which the power output (135–190 mW m<sup>-2</sup>) is greater than most soft and green power sources reported previously.

Sodium alginate (SA) was used as the polyanion,<sup>[26]</sup> while chitosan, a bio-waste, was dissolved in the aqueous hydrochloric acid solution to obtain a low viscosity colloid as the polycation (Figure 1a[iii],b and Figure S1, Supporting Information).<sup>[27,28]</sup> After the coacervation reaction, the SA solution is transformed into the polyelectrolyte hydrogel with two inverse ends. To visualize the dynamic colloid diffusion and coacervation reaction, a dyed chitosan colloid was observed to self-propagate into the SA solution which gradually transferred into a polyelectrolyte hydrogel and formed two distinct regions (Figure S2a and Movie S1, Supporting Information). Engineered using directink-writing, such polyelectrolyte hydrogels can be readily manufactured with high design flexibility and diverse geometry on a large scale (Figure S2b, Supporting Information). The stressstrain curve revealed that the hydrogels possess a stretchability of ≈25% with a SA concentration-dependent strength relationship, where the strength is observed to increase with the concentration of SA solution (Figure S3, Supporting Information).

To verify the hypothesis that the passive and dynamic behaviors are orchestrated in one hydrogel, we started with different

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**Figure 2.** Ionic electroresponse of polyelectrolyte hydrogels. a) *I–V* curve of the hydrogel with a bias from –1 to 1 V. The inset is the plot of absolute current as a function of bias. b) Schematic diagram of electroresponse in the hydrogel with cathode water contact. c,d) Open-circuit voltage response of the hydrogel under external stimuli of water and artificial sweat, respectively. e) Schematic diagram of electroresponse in the hydrogel with anode salt solution contact. f) Open-circuit voltage response of hydrogel under external stimuli of a variety of alkali metal chloride solutions (1 M of LiCl, NaCl, and KCl). g,h) Open-circuit voltage response of the hydrogel under external stimuli of artificial sweat and water, respectively. i) Effects of the SA and chitosan ratio and SA concentration on the open-circuit voltage. j) Effect of HCl concentration in chitosan colloid on open-circuit voltage of the hydrogels (5 wt% SA) and a volume ratio of SA and chitosan of 3:2.

salt solutions considering the diverse external ions stimuli, including water, alkali chloride solution (1  $\[mmm]$  of LiCl, NaCl, and KCl), as well as artificial sweat mimicking the epidermal perspiration. In the *I*–V curve, the short-circuit current of hydrogel was obtained when the bias is close to zero (**Figure 2a**). The short-circuit current is  $\approx 0.4 \[mmm]$ A. The inset shows the absolute current as a function of the bias, where the asymmetric plot demonstrates the presence of electric potential in the hydrogel. Owing to the presence of a built-in electric field and potential between the two ends, the voltage corresponding to the minimum current in the inset is slightly higher than the open-circuit voltage. To study the selective response of the bio-hydrogel, the cathode of the hydrogel is placed in contact with the water

and salt solution, accordingly (Figure 2b). As the cathode touched the water, the open-circuit voltage of hydrogel presented a swift rise and then underwent a slight increase. The open-circuit voltage noticeably reverted to the original state once it is displaced from the water (Figure 2c). Conversely, the artificial sweat and alkali chloride solutions negatively stimulated the cathode, yielding a sharp drop in the voltage (Figure 2d and Figure S4, Supporting Information). Importantly, the voltage was able to recover rapidly after removing it from the salt solutions (Figure S4, Supporting Information). Subsequently, the performance of the hydrogel anode was also evaluated under the same external stimuli (Figure 2e). The inherent virtue is that the external stimuli hardly influence the other end of the



uncontacted hydrogel cathode. These hydrogels showed a different extent of positively differentiated electroresponse under various alkali chloride solutions (1 M), owing to the disparate radii of alkali ions.<sup>[29-34]</sup> Once the alkali chloride solutions were withdrawn, the raised voltages generally resumed the original state. The only exception was the voltage of hydrogel stimulated by the LiCl solution as it cannot restore completely until the addition of the water. This likely ascribes to the residual of Li ions (Figure 2f). Moreover, the voltage of the bio-hydrogel measured in the LiCl solution is greater than that in NaCl and KCl solutions, mainly due to the lower diffusion rate of Li ions in comparison with the Na and K ions. However, there is a fine difference between the voltage output measured in NaCl and KCl solutions, probably attributed to the closeness in radii and diffusion rates between the hydrated Na and K ions. The hydrogel, as expected, presented a declining and rising voltage when the anode was contacted with water and artificial sweat, respectively (Figure 2g,h). This differentiated electroresponse to salt media and water is the bio-inspired analogical design corresponding to the dynamic ionic selectivity in the cytomembrane.

To further study hydrogels governed by the self-propagative flow approach, the effects of SA concentrations, the volume ratio between SA solution and chitosan colloid, as well as the concentration of HCl in chitosan colloid on ionic transport were established (Figure 2i,j). Increasing the volume ratio of SA to chitosan was shown to improve the open-circuit voltage at SA concentration below 10 wt%. However, it has no obvious effect on the open-circuit voltage as the SA concentration reached 10 wt%. At this concentration, the bio-hydrogels possess a slightly lower exciting voltage in comparison with the hydrogels with 5 wt% SA (Figures S5 and S6, Supporting Information).

For most bio-inspired artificial soft power sources demonstrated thus far, the energy output is intermittent and low-grade while the polyelectrolyte bio-hydrogels in this work are capable of continuous and high-power output. In terms of performance as a soft power source, the polyelectrolyte hydrogels with 5 wt% SA can generate a power density of 135–190 mW m<sup>-2</sup> with an external resistance of 0.2–10 M $\Omega$  (Figure 3a), superior to most bio-inspired soft and green power sources (Figure 3b).<sup>[9,18–20,34–41]</sup> A reduced HCl concentration (1.2 M) was able to boost the voltage (0.17 ± 0.03 V) and power density (≈190 mW m<sup>-2</sup>) in the bio-hydrogel, while the bio-hydrogels with 5 wt% SA and 2.2 M HCl show a fast recovery to the excited state and higher short-circuit current (Figures S7 and S8, Supporting Information). Thus, bio-hydrogels with 5 wt% SA were chosen for further study.

The long-term performance of bio-hydrogels with the cathode in contact with water was monitored in the surroundings (Figure 3c,d and Figure S9, Supporting Information). The addition of water to the bio-hydrogel boosted the open-circuit voltage and sustained the output even after a certain shelf life. The fine fluctuation in the voltage signal was attributed to the surrounding changes, such as the temperature, humidity, pressure, as well as velocity of wind, indicating that the water evaporation rate could dominate the voltage (Figures S10 and S11, Supporting Information). As expected, the unremitting voltage output of the cathode hydrogel is also validated for the LiCl medium (Figure S12, Supporting Information). This further demonstrates that such polyelectrolyte hydrogels can

selectively electro-respond to the salt media and water, as well as generate energy as a soft power source. The voltage and current of hydrogels will be attenuated when supplying highpower energy. The current reduces once it short-circuits. However, the current will reach a plateau when the input power can offset the output power (Figure 3e and Figure S13, Supporting Information). After removing the load, the voltage and current can recover quickly (Figure S7c, Supporting Information). When outputting low-power energy, the hydrogel can supply energy steadily (Figure S7c, Supporting Information). To study the current change under stimuli of salt media and water, the internal resistance was measured further (Figure S14, Supporting Information). The results revealed that there is no obvious difference between the resistance of hydrogels in air and stimuli (water and salt media) in Figure S14a-d, Supporting Information. Thus, the voltage increases under stimuli indicates the increased current. Furthermore, the short-circuit current of the hydrogel after 2500 s is boosted under water stimuli (Figure S14e, Supporting Information).

To characterize the stability of the bio-hydrogels in different medium solutions, they were immersed in a variety of solutions for 2 days (Figure 3f). The hydrogels did not noticeably change in water (Figure 3f insets), alkali chloride solutions (1 M), and even in 0.1 M HCl, except when it is submerged in 0.1 M NaOH (Figure S15, Supporting Information). With an increased concentration of LiCl solution from 1 to 5 M, the hydrogels display consistent structural stability while the output voltage is reduced with LiCl concentration (Figure 3g), owing to the reduced diffusion rate of chloric and hydrated lithium ions upon their concentration,<sup>[42]</sup> revealing the concentration-dependent electroresponse in these hydrogels.

To elucidate the underlying mechanism of ionic selectivity and unremitting voltage output, we examine the in situ surficial potential distribution in conjunction with constructing an asymmetric model based on the theoretical derivation and performing molecular dynamics (MD) simulation on the biohydrogel (Figure 4). When adding the hydrochloric acid to dissolve the chitosan, the amide groups are protonated, yielding positively charged.<sup>[27,28,43]</sup> During the coacervation reaction, hydrochloric acid diffuses into SA solution along with the chitosan colloids, transforming into a gradient-structured alginate acid hydrogel. The residual SA, far away from the chitosan colloid, remains negatively charged, of which sodium, chloride ions, and protons are deemed as the charge carriers in the asymmetric hydrogels (Figure 4a and Equations S1-S3 and Figure S16, Supporting Information). In the case of the asymmetric hydrogels, the rich chitosan region denotes a positively charged cathode, while the rich SA region depicts a negatively charged anode with a higher energy level relative to the cathode (Figure 4b). The surficial potential difference (SPD) characterization was performed at two test sites (i) and (ii) in Figure 4b to validate the potential difference between the cathode and anode, respectively (Figure 4c). The results revealed that there is an SPD of ≈0.14 V in the hydrogel induced by the asymmetric structure, close to the open-circuit voltage of the hydrogel. To validate the asymmetric structure induced by the self-propagative flow, Fourier transform infrared (FTIR) spectroscopy of pristine SA, chitosan, as well as the two test sites (i and ii) of hydrogel were studied (Figure 4d and Figure S17, Supporting www.advancedsciencenews.com

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**Figure 3.** Unremitting energy output performance in polyelectrolyte hydrogel. a) Open-circuit voltage, current density, and power density as a function of the external resistance. b) Power density and current density of our hydrogels and other soft power sources reported previously that are stimulated by the humidity or humidity gradient.<sup>[9,18–20,34–40]</sup> Here, samples 1.2 and 2.2 represent the hydrogels fabricated using chitosan colloids with 1.2 and 2.2 M HCl, respectively. c,d) Long-term performance of hydrogel with HCl concentration of  $\approx$ 2.2 M after several days in between breaks under external stimuli of water in an open ambient. e) Short-circuit current ( $I_{sc}$ ) of hydrogels as a function of time; 1) time from 0 to 2000 s; 2) enlarged view of time from 0 to 10 s; 3) enlarged view of time from 100 to 500 s. f) Stability test of bio-hydrogels in various solutions containing water, NaCl (1 M), LiCl (1 M), KCl (1 M), HCl (0.1 M), and NaOH (0.1 M) solutions. The insets are the digital photographs of the hydrogel immersed in water before and after 2 days. g) Effect of LiCl concentration on voltage change ( $\Delta V/V_0$ ) in the hydrogel.

Information). In FTIR spectra of hydrogels, the absorption peak at 1729 cm<sup>-1</sup> corresponds to the stretching mode of C=O in carboxylic acid (–COOH) of alginate acid while the absorption peak at 1522 cm<sup>-1</sup> designates as amide II and symmetric –NH<sub>3</sub><sup>+</sup>. These peaks are regarded as testing peaks. The absorption peaks at 1629 cm<sup>-1</sup> of water are deemed as the reference peaks.<sup>[44-46]</sup> The intensity ratios ( $\alpha$ ) of testing peaks with respect to reference peaks at site (i) ( $\alpha_{COOH}$ : 1.15;  $\alpha_{NH}$ : 0.21) are greater than these ( $\alpha_{COOH}$ : 0.98;  $\alpha_{NH}$ : 0.12) at site (ii), illuminating the presence of a compositional gradient in these asymmetric hydrogels.

Based on the above results, we hypothesize that the differentiated electroresponse upon alkali metal ions is dominated by their diffusion rates ( $\dot{D}$ ) and charges. To corroborate this hypothesis, we first constructed the molecular diffusion model that described the self-propagation reaction in polyelectrolyte hydrogels (Figure 4e and Movie S2, Supporting Information). After the reaction, the chitosan infiltrated with SA to form the cathode, narrow transition, and anode regions. The chitosan chains show the highest diffusion rate ( $D_{zz}$ ) in the parallel (*zz*) diffusion direction as opposed to *xx* and *yy* directions (Figure 4f). We subsequently simulated the diffusion of alkali metal ions into polyelectrolyte hydrogels from the SA and chitosan ends, respectively (Figure 4g and Movies S3 and S4, Supporting Information). The results demonstrated that the different diffusion rates in alkali metal ions were induced







**Figure 4.** Mechanism of differentiated ionic electroresponse in polyelectrolyte hydrogel. a) Schematic diagram of the self-propagation. b) Functional group distribution and corresponding energy level (*E*) in the asymmetric hydrogels. Energy difference ( $\Delta E$ ) equals the energy level of SA ( $E_{SA}$ ) minus that of chitosan ( $E_{Chi}$ ). c) Surface potential difference of asymmetric hydrogel at two test sites in (b). d) FTIR spectra of the asymmetric hydrogel at two test sites. e) Molecular dynamics (MD) simulation of the self-propagation flow. f) Calculated diffusion mean-square displacements (MSD) of chitosan molecules in different directions. g) MD simulation of ion diffusion. h) Diffusion rates of cations and corresponding anions at the interface between sodium alginate and salt media.

by the diverse radii of their hydrated ions.<sup>[30,31,33,34]</sup> When the anode contacted the alkali metal media, the anions with a high diffusion rate accumulate at the interfaces between anode and salt media driven by the diffusion effect and capillary effect, causing the improved potential difference (Figure 4h). Owing to the negative charges from the carboxyl groups, anions hardly diffuse into the hydrogel in a short time, beneficial in regaining the rest state after removal of the salt media (Figure 4h,i). The low diffusion rates of the hydrated ions result in a dynamic accumulation (Tables S1 and S2, Supporting Information) occurring at the interface,<sup>[47,48]</sup> where hydrated lithium ions are less than that of hydrated sodium and potassium ions owing to their divergent hydration radii, which leads to the differential voltageresponse upon diverse salt media. The fine potential difference induced by sodium and potassium ions is attributed mainly to their diffusion rates and that of corresponding anions.<sup>[49,50]</sup> By contrast, when the water diffuses into the anode, the charge carriers (Na<sup>+</sup> from SA and Cl<sup>-</sup> from the self-diffusion reaction) in hydrogel migrate with water flow. Cl-, as a water structure breaking ion, moves faster than Na<sup>+</sup> (water structure making ion), leading to the drop in the negative potential of anode and the decrease of potential difference.<sup>[49,51,52]</sup> When water contacts the cathode, the main carriers, Cl-, diffuse away with water flow and improve the positive potential of the cathode. Once the alkali ions contact the cathode, the anions diffuse fast and accumulate at the interfaces quickly, driven by both diffusion and electrostatic interactions to reduce the potential difference (Tables S3 and S4, Supporting Information). The voltage change could be affected by the ion concentration gradient based on the Nernst theory. However, the  $\Delta V$  is observed to decrease with the Li-ion concentration (Figure 3f) and, evidently, the  $\Delta V$  is diverse under the stimuli of different ions (Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) of the same concentration (Figure 2f). Taken together with the simulation results presented in Figure 4e–i, the  $\Delta V$  should be dominated mainly by the diffusion rates of ions. The dynamic surficial potential under water stimulus was recorded, which further verifies the electroresponse of hydrogels (Figure S18, Supporting Information).

In addition, the crystallinity of pure SA, chitosan, and hydrogels was characterized (Figure S19, Supporting Information). www.advancedsciencenews.com



**Figure 5.** Manufacture and performance of direct-writing hydrogel via 3D printing in parallel and series models. a) Direct-ink-writing process of hydrogel fibers. b) Schematic diagram of coacervation reaction in direct-ink-written hydrogel fiber. c) Patterns of printed hydrogels containing (i) isolated droplets, (ii) continuous zig–zag, and (iii) spiral. Scale bar: 1 cm. d) Long-term stability of open-circuit voltage of droplet hydrogel exposed to water. Here, the dotted curve is the smooth curve of the original black curve. e) *I–V* curves of the direct-ink-written hydrogel fibers. The inset shows the plots of their open-circuit voltage with time in natural surroundings. f) Open-circuit of seven hydrogel units in series with a time. g,h) Output characteristic ( $I_C-V_{EC}$ ) curves as a function of forward and reverse input voltage ( $V_{EB}$ ) of a p–n–p ionic transistor.

The reduced intensity of the peak at  $\approx 21^{\circ}$  revealed the disordering of SA polymer chains, while chitosan samples show a decreased peak intensity at  $\approx 20^{\circ}$  with addition of HCl, indicating that HCl lowers the crystallinity of chitosan. These reduced crystallinities and addition of HCl are favorable to improve the mobility of counter ions and current in bio-hydrogels (Table S5, Supporting Information), further suggesting the regulable current of the bio-hydrogels with diverse design parameters including concentrations of SA and HCl as well as ratios between SA and chitosan.

Next, we demonstrated a straightforward means to manufacture diverse hydrogel architectures in tandem with self-activated gradient profiles. By bringing the design and fabrication of the polyelectrolyte hydrogels closer to a scalable production, we are able to further improve their modularized energy generation performance. SA solution was direct-ink-written using a 3D printer on a recyclable paper substrate that was pre-coated by chitosan colloid (**Figure 5**a,b). By undergoing a bottom-up self-propagative flow, spatiotemporal hydrogel structures were effortlessly fabricated with three basic topological geometries, including isolated droplets, continuous zig-zag, and spiral fibers (Figure 5c[i-iii] and Movies S5-S7, Supporting Information). Benefitting from the flexible transferability, the hydrogel fibers can be conceivably transferred onto a variety of electrodes, such as the flexible and hydrophilic carbon cloth inert electrode (Figure 5c[iii]). The longterm performance of 3D printed droplet hydrogel was studied (Figure 5d), and presented a voltage output of  $\approx$ 125 mV, on a par with the single hydrogel in Figure 2. As expected, the parallel hydrogel configuration displayed a higher short-circuit current (30 µA) and an open-circuit voltage (≈100–110 mV) in comparison with the above-demonstrated single hydrogel (Figure 5e). To demonstrate scalable energy generation, seven hydrogels are connected in series in a modularized format which showed an open-circuit voltage of more than 1 V, consistent with the theoretical value (Figure 5f and Figure S20, Supporting Information). This demonstration reveals the potential of scalability of these bionic hydrogels via 3D printing and auto-initiated chemical graded soft energy generation system.

It is envisaged that the provision of additive manufacturing and self-propagative design principle of the bio-hydrogel will



lead to potential practical applications. As such, proof-of-concept demonstration rather than optimized designed ionic bipolar junction transistors were fabricated with diverse geometries, and subjected to applying the direct-current biases (Figure 5g,h and Figures S21 and S22, Supporting Information). Under reverse bias, the n-p-n ionic bipolar junction transistors show a rectifying current with a ratio from 1.1 to 1.4. In the case of p-n-p ionic bipolar junction transistors, the collector current decreased with the increasing bias between emitter and base, yielding a rectification of 40–160 under forward and reverse bias, respectively. The thermo-diffusion-induced voltage change of polyelectrolyte hydrogels was studied in the temperature difference from 0 to 40 K (Figure S23, Supporting Information). The thermopower of such hydrogels is  $\approx 2.2 \text{ mV K}^{-1}$  with an electrical conductivity of  $\approx 0.1 \text{ S m}^{-1}$ , superior to most of thermoelectric devices.<sup>[53,54]</sup>

The work presented here introduces the orchestration of a differentiated ionic electroresponse and delivering of an unremitting artificial power source based on nature-inspired designing of upcycled bio-hydrogel in analogy to the cytomembrane. By deploying the atypical self-propagative asymmetric architecture and scale-up manufacturing, these bio-hydrogels are able to generate a power density of 135-190 mW m<sup>-2</sup> per unit, superior to most soft and green power sources, and a voltage of 1 V in a series of seven units, approaching the applicable power level for low power-consumption devices.<sup>[9]</sup> The design concept employed in this work is an exemplar of integrative design to deliver a dynamic differentiated electroresponse and passive unremitting power output, paving a way to bridge the gap between artificial devices and organic physiological behavior. Potentially, this work can be adopted for self-powering implants, wearable health monitors, or soft power sources for selective neural excitation or inhibition which is much sought after for biomedical application.<sup>[25]</sup>

#### 2. Experimental Section

Synthesis of Polyelectrolyte Hydrogel: SA (powder, Sigma-Aldrich) was dissolved into DI water with concentrations of 5, 8, and 10 wt%. After stirring overnight at room temperature (RT), the clear yellow SA solution was obtained. 0.75 g of chitosan (medium molecular weight, 15 000–31 000 Da., Sigma-Aldrich) was dispersed into an aqueous hydrochloric acid solution with 5 mL of HCI and 45 mL of DI water. After stirring for 30 min at RT, the chitosan dispersion was kept at 70 °C for 20 min to obtain a slightly yellow solution where the amino groups of chitosan were protonated completely. Subsequently, 5 mL of HCI was dropped into the protonated solution for 2 min with vigorous stirring until a white colloid was obtained at RT.

SA solution was first poured into a polydimethylsiloxane (PDMS) mold and then the chitosan colloid was added from the other end of the mold until the mold was filled. The SA/chitosan hydrogel, called polyelectrolyte hydrogel, was obtained after the white chitosan colloid became transparent after 10 h. The volume ratio of SA solution to chitosan colloid was controlled with 3:2, 1:1, and 2:3.

Material Characterization: The *I*–V curves and open-circuit voltage of the hydrogels were performed using an electrochemical workstation (CHI660E) and the hydrogels were conducted using carbon fibers as inert electrodes to avoid oxygen absorption and electrochemical corrosion. In order to eliminate the capillary effect of carbon fibers on the electric signal, silver paste (SPI Supplied, Structure Probe, Inc.) was cast in the middle of carbon fibers and the optical image of carbon fiber was shown in Figure S24, Supporting Information. Before measurement, the

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hydrogels were activated to promote the mobility of counter ions with a bias from -1 to 1 V for three times and then short-circuited to discharge for several seconds after washing for three times. The work electrode was always connected with the chitosan end without notice. The resistance of SA solution and hydrogels was tested with silver electrodes in a PDMS mold using TH2830 LCR Meter (Tonghui) (Figure S25 and Tables S6 and S7, Supporting Information). Stress-strain curves of hydrogels were performed on an electronic universal testing machine (CMT6103, MTS Systems Co., Ltd.). The surficial potential was probed by Kelvin probe force microscope (KPFM) measurement on a commercial scanning probe microscopy system (MPF-3D, Asylum Research, Oxford Instrument) with a conductive Pt-coated silicon tip (AC240 PP, Olympus). For KPFM, a double-passing scheme with a height of 40 nm was performed to minimize the topographic crosstalk. The crystal structure of samples was studied by X-ray diffraction, collecting the diffraction patterns using a diffractometer (Bruker AXS) equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.54$  Å). FTIR spectroscopy of samples was conducted on a Shimadzu IR Prestige-21 spectrophotometer, multi-scanning 40 times in the range of 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The hydrophilia of carbon cloth (WOS1009, CeTech) was executed using a plasma (Harrick Plasma, Inc.) with a power of 45 W for 3 min. Optical images of samples were performed on optical microscopy (Olympus BX53M). The artificial sweat was composed of NaCl (0.34  $\mu$ ), ammonium chloride (NH<sub>4</sub>Cl, 0.33 м), urea (0.083 м), acetic acid (0.041 м), and lactic acid (0.17 м). The thermo-diffusion-induced performance of hydrogels was characterized using a Keithley 2602 System Source Meter. The temperature difference was supplied by two thermoelectric modules, supplied by a dual channel DC power supply (EL302RD Dual Power Supply).

Molecular Dynamic Simulation: To understand the intra-molecular interaction between SA solution and chitosan colloid, MD simulations were performed. To this end, the monomers of SA and chitosan polymers were optimized by employing the Dmol<sup>3</sup> package with the Perdew-Burke-Ernzerhof functional. Polymer chains of SA and chitosan were then constructed with 30 and 20 monomers, respectively. Two systems involving 20 SA chains and 15 chitosan chains, respectively, were solvated with water, and the systems were relaxed under the constant-temperature, constant-pressure ensemble (N, P, T) with periodic boundary conditions. MD simulations were carried out using the Forcite module in Materials Studio software (Accelrys Software Inc.). The ab initio optimized COMPASS force field which had been validated and popularly selected for describing condensed systems, was adopted to calculate inter/intra-molecular forces. After obtaining stable configurations of SA solution and chitosan colloid, two systems were set adjacently and the combined system consisting of  $\approx 60\ 000$ atoms was run for 600 ps under the canonical ensemble (N, V, T), to study the diffusion dynamics of chitosan molecules at the interface. The temperature of the system during MD simulations was maintained at 298 K by a Nosé-Hoover thermostat, and vacuum layers outside the combined system in the normal direction to the interface were set to avoid image interactions. Periodic boundary conditions were used in the lateral directions, and SA molecules were fixed to save computational cost. The time step was set to 1.0 fs and the cut-off distance was 1.25 nm. The diffusion coefficient of chitosan molecules was obtained through the Einstein relation,  $D = \lim_{t \to \infty} \frac{\langle r^2 \rangle}{mt}$ , where m = 4 for 2D and 6 for 3D cases and  $\langle r^2 \rangle$  use the user 3D cases, and  $\langle r^2 \rangle$  was the mean square displacement.

After obtaining the SA-chitosan composites, additional MD simulations were performed to study dynamics of salt media in the SA-chitosan composites. A system consisting of 1  $\,$  XCl solution (X = Li, Na, or K), was relaxed under NPT ensemble and then was located close to the composites to investigate the ion diffusion. The simulations were run on both sides of the composites, that is, SA and chitosan side; ion diffusion coefficients were also calculated with the Einstein relation.

*Printing*: The morphology of hydrogels was carried out via 3D printing. The filter paper was first infiltrated using the chitosan colloid (3 mL) and then the SA solution was extruded on the filter paper as the substrate, guided by the G-code program. The thickness and height of hydrogels were tailored by the extruding rate and moving rate.

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## **Supporting Information**

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

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#### **Conflict of Interest**

The authors declare no conflict of interest.

## **Author Contributions**

X.P. and Y.J. contributed equally to this work. G.W.H. proposed the research direction and supervised the project. X.P. designed the experiments, analyzed the data, and wrote the draft. Y.J. and X.P. conducted to the MD simulation and data analysis. Y.Z. and X.-Q.W. (Present address: Soochow University) helped to discuss and design graphs. W.L. conducted AFM characterization. G.W.H., X.P., and J.H. revised the manuscript. All authors participated in the discussion and reviewed the manuscript before submission.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

#### Keywords

bio-hydrogels, electroresponses, ionic selectivity, salt media, unremitting outputs, water

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- [1] T. C. Cheung, M. W. Steinberg, L. M. Oborne, M. G. Macauley, S. Fukuyama, H. Sanjo, C. D'Souza, P. S. Norris, K. Pfeffer, K. M. Murphy, M. Kronenberg, P. G. Spear, C. F. Ware, Proc. Natl. Acad. Sci. U. S. A. 2009, 106, 6244.
- [2] M. Riegman, M. S. Bradbury, M. Overholtzer, Trends Cancer 2019, 5, 558.
- [3] D. V. Krysko, L. Leybaert, P. Vandenabeele, K. D'Herde, Apoptosis 2005, 10, 459.
- [4] L. Lu, S. Qian, P. A. Hershberger, W. A. Rudert, D. H. Lynch, A. W. Thomson, J. Immunol. 1997, 158, 5676.
- [5] M. Voelker, P. Fromherz, Small 2005, 1, 206.
- [6] T. M. Jessell, E. R. Kandel, Neuron 1993, 72, 1.
- [7] L. E. McElvain, M. Faulstich, J. M. Jeanne, J. D. Moore, S. du Lac, Neuron 2015, 85, 1132.

#### www.advenergymat.de

- [8] K. C. Catania, Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 6979.
- [9] T. B. H. Schroeder, A. Guha, A. Lamoureux, G. Vanrenterghem, D. Sept, M. Shtein, J. Yang, M. Mayer, Nature 2017, 552, 214.
- [10] M. London, A. Schreibman, M. Haä;usser, M. E. Larkum, I. Segev, Nat. Neurosci. 2002, 5, 332.
- [11] R. F. Rakowski, D. C. Gadsby, P. De Weer, J. Membr. Biol. 1997, 155, 105
- [12] J. P. Morth, B. P. Pedersen, M. S. Toustrup-Jensen, T. L. M. Sørensen, J. Petersen, J. P. Andersen, B. Vilsen, P. Nissen, Nature 2007, 450, 1043
- [13] T. Gonen, T. Walz, Q. Rev. Biophys. 2006, 39, 361.
- [14] H. Ogawa, T. Shinoda, F. Cornelius, C. Toyoshima, Proc. Natl. Acad. Sci. U. S. A. 2009, 106, 13742.
- [15] E. Gouaux, R. Mackinnon, Science 2005, 310, 1461.
- [16] M. V. Brown, Electr. Eng. 2013, 69, 145.
- [17] F. Zhao, Y. Liang, H. Cheng, L. Jiang, L. Qu, Energy Environ. Sci. 2016. 9. 912.
- [18] H. Wang, T. He, X. Hao, Y. Huang, H. Yao, F. Liu, H. Cheng, L. Qu, Nat. Commun. 2022, 13, 2524.
- [19] H. Wang, Y. Sun, T. He, Y. Huang, H. Cheng, C. Li, D. Xie, P. Yang, Y. Zhang, L. Qu, Nat. Nanotechnol. 2021, 16, 811.
- [20] T. Xu, X. Ding, Y. Huang, C. Shao, L. Song, X. Gao, Z. Zhang, L. Qu, Energy Environ. Sci. 2019, 12, 972.
- [21] J. Bai, Y. Huang, H. Wang, T. Guang, Q. Liao, H. Cheng, S. Deng, Q. Li, Z. Shuai, L. Qu, Adv. Mater. 2022, 34, 2103897.
- [22] Y. Huang, H. Cheng, C. Yang, P. Zhang, Q. Liao, H. Yao, G. Shi, L. Ou, Nat. Commun. 2018, 9, 4166.
- [23] X. Nie, J. Bingxue, N. Chen, Y. Liang, Q. Han, L. Qu, Nano Energy 2018, 46, 297.
- [24] W. Lu, T. Ding, X. Wang, C. Zhang, T. Li, K. Zeng, G. W. Ho, Nano Energy 2022, 104, 107892.
- [25] Y. Huang, Y. Cui, H. Deng, J. Wang, R. Hong, S. Hu, H. Hou, Y. Dong, H. Wang, J. Chen, L. Li, Y. Xie, P. Sun, Nat. Biomed. Eng. 2022, https://doi.org/10.1038/s41551-022-00931-0.
- [26] H. Cui, N. Pan, W. Fan, C. Liu, Y. Li, Y. Xia, K. Sui, Adv. Funct. Mater. 2019, 29, 1807692.
- [27] M. Rinaudo, G. Pavlov, J. Desbrières, Polymer 1999, 40, 7029.
- [28] M. Rinaudo, G. Pavlov, J. Desbrières, Int. J. Polym. Anal. Charact. 1999, 5, 267.
- [29] S. B. Rempe, L. R. Pratt, J. Am. Chem. Soc. 2000, 122, 966.
- [30] J. Peng, D. Cao, Z. He, J. Guo, P. Hapala, R. Ma, B. Cheng, J. Chen, W. J. Xie, X. Z. Li, P. Jelínek, L. M. Xu, Y. Q. Gao, E. G. Wang, Y. Jiang, Nature 2018, 557, 701.
- [31] S. Imberti, A. Botti, F. Bruni, G. Cappa, M. A. Ricci, A. K. Soper, I. Chem. Phys. 2005, 122, 194509.
- [32] A. Bankura, V. Carnevale, M. L. Klein, J. Chem. Phys. 2013, 138, 014501.
- [33] A. Grossfield, J. Chem. Phys. 2005, 122, 024506.
- [34] S. Varma, S. B. Rempe, Biophys. Chem. 2006, 124, 192.
- [35] P. Li, N. Su, Z. Wang, J. Qiu, ACS Nano 2021, 15, 16811.
- [36] S. Zheng, J. Tang, D. Lv, M. Wang, X. Yang, C. Hou, B. Yi, G. Lu, R. Hao, M. Wang, Y. Wang, H. He, X. Yao, Adv. Mater. 2022, 34, 2106410.
- [37] Y. Huang, H. Cheng, C. Yang, H. Yao, C. Li, L. Qu, Energy Environ. Sci. 2019, 12, 1848.
- [38] C. Liu, S. Wang, X. Wang, J. Mao, Y. Chen, N. Fang, S.-P. Feng, Energy Environ. Sci. 2022, 15, 2489.
- [39] X. Liu, H. Gao, J. E. Ward, X. Liu, B. Yin, T. Fu, J. Chen, D. R. Lovley, J. Yao, Nature 2020, 578, 550.
- [40] J. Tan, S. Fang, Z. Zhang, J. Yin, L. Li, X. Wang, W. Guo, Nat. Commun. 2022, 13, 3643.
- [41] Y. Zhang, K. Shang, F. Guo, Y. Shang, S. Chang, L. Cui, X. Lu, J. Zhou, C. Fu, Q. He, Nat. Commun. 2022, 13, 3484.
- [42] M. B. Singh, V. H. Dalvi, V. G. Gaikar, RSC Adv. 2015, 5, 15328.

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- [43] Q. Z. Wang, X. G. Chen, N. Liu, S. X. Wang, C. S. Liu, X. H. Meng, C. G. Liu, *Carbohydr. Polym.* **2006**, *65*, 194.
- [44] G. Lawrie, I. Keen, B. Drew, A. Chandler-Temple, L. Rintoul, P. Fredericks, L. Grøndahl, *Biomacromolecules* 2007, *8*, 2533.
- [45] A. Pawlak, M. Mucha, Thermochim. Acta 2003, 396, 153.
- [46] M. L. Duarte, M. C. Ferreira, M. R. Marvão, J. Rocha, Int. J. Biol. Macromol. 2002, 31, 1.
- [47] M. McEldrew, Z. A. H. Goodwin, A. A. Kornyshev, M. Z. Bazant, J. Phys. Chem. Lett. 2018, 9, 5840.
- [48] J. Vatamanu, O. Borodin, J. Phys. Chem. Lett. 2017, 8, 4362.
- [49] S. Reiser, S. Deublein, J. Vrabec, H. Hasse, J. Chem. Phys. 2014, 140, 044504.
- [50] J. Mähler, I. Persson, Inorg. Chem. 2012, 51, 425.
- [51] S. H. Lee, J. Phys. Chem. 1996, 100, 1420.
- [52] S. H. Lee, Mol. Simul. 1994, 101, 6964.
- [53] T. Ding, Y. Zhou, X. Q. Wang, C. Zhang, T. Li, Y. Cheng, W. Lu, J. He, G. W. Ho, Adv. Energy Mater. 2021, 11, 2102219.
- [54] T. Ding, K. H. Chan, Y. Zhou, X. Q. Wang, Y. Cheng, T. Li, G. W. Ho, *Nat. Commun.* 2020, 11, 6006.