Polyelectrolyte hydrogel: A versatile platform for mechanical-electric conversion and self-powered sensing

Xiaofeng Pan [a], Qinhua Wang [b,c], Daniele Benetti [a,*], Yonghao Ni [b,d,**], Federico Rosei [a,*]

[a] Centre for Energy, Materials and Telecommunications, Institut National de la Recherche Scientifique, 1650 Boulevard Lionel-Boulet, Varennes, Québec J3X 1P7, Canada
[b] College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou City, Fujian Province 350002, People's Republic of China
[c] Department of Chemistry, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montréal, Québec H3C 3J7, Canada
[d] Limerick Pulp and Paper Centre, Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick E3B5A3, Canada

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ABSTRACT

There is an urgent need to develop self-powered technologies for portable strain/pressure sensors. In this work, inspired by salinity-gradient electricity generation, we report the design and fabrication of a mechanical-electric conversion and self-powered sensing platform based on polyelectrolyte hydrogels. Using polyacrylic acid (PAA, whose -COOH group can ionize H^+ in water) hydrogel as a model system, we observe that the compression deformation process of the hydrogel leads to a localized increase in the H^+ concentration, that induces a directional H^+ diffusion as a result of ion concentration difference. In contrast, the PAA chain (negatively charged), as a hydrogel backbone, is hindered from moving freely due to the locking of the hydrogel network. Such drastic difference between ionized H^+ and fixed PAA chain defines an opportunity for converting mechanical energy into electricity by compressing the PAA hydrogel. The good elasticity of the PAA hydrogel allows us to repeatedly regenerate and fully recover the electrical signal and finally completes the recycle sensing (>1000 s). PAA hydrogels have also been shown to convert static or low frequency (~0.05 Hz) pressure (0.05–5 N) to output direct voltage/current. In particular, the hydrogel can yield a voltage output up to ~6 mV and a current of ~2 μA when the pressure is 5 N. Taking full advantage of the special sensing principle, we have developed both self-powered and temperature-insensitive PAA hydrogel-based position recognizers and multi-dimensional sound detectors. Importantly, this mechanical-to-electric conversion concept is also applicable to other polyelectrolyte hydrogels. This simple and low-cost soft material system is promising for applications in sensing and energy harvesting.

1. Introduction

Polymer hydrogels are being widely studied for use in portable pressure sensors and electronic skins [1–4]. Due to their high water content and adjustable mechanical properties, polymer hydrogels can perfectly match the tissues of the skin to achieve both high biological and mechanical compatibility [5–7]. In addition, thanks to its structural versatility the hydrogel system can be pre-doped and adjusted with unique functions and macro/microstructural characteristics [8–11].

Polymer hydrogels can combine the great elastic properties of polymers with the electric-signal transport channel of conductive media [12–14]. This type of hydrogel-based sensor can induce the redistribution of the conductive channel and the subsequent adjustment of electrical signals through compression and stretching of the internal polymer network, so as to respond to external mechanical stimuli [15,16]. Commonly, conductive nano-metals, intrinsically conductive polymers, and carbon materials are used as conductive fillers [17]. However, conductive fillers present several issues, such as easy aggregation, high-cost, challenging synthesis, and opacity of the hydrogel that hinder their use in wearable electronics [13,18,19]. Moreover, ionic conductive hydrogels are prone to ion leakage, which could present health hazards for the human body [20,21]. In contrast, low-cost polyelectrolyte (high molecular weight polymer) hydrogels are polymerized and assembled by ionizable monomers or natural polysaccharide in

* Corresponding author.
** Corresponding author at: College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou City, Fujian Province 350002, People's Republic of China.
E-mail addresses: daniele.benetti@inrs.ca (D. Benetti), yonghao@unb.ca (Y. Ni), federico.rosei@inrs.ca (F. Rosei).

water, exhibit sufficient conductivity and do not leak [22].

In addition, most hydrogel sensors have to rely on an external rigid power source to operate, so that portable hydrogel electronics requires the realization of self-powered pressure sensing [23–27]. Generally, the assembly of hydrogels into nano-triboelectric generators (TENG) results in high self-powered performance, yet there are obstacles such micro-structural preparation and high cost [28,29]. In addition, TENG's contact separation detection method affects the universality of signal recognition.[30–32].

It is known that a salt concentration gradient-driven ion selective permeation membrane can trigger the directional transport of a single ion (cation or anion), which leads to the generation of electrical power [33–35]. Polyelectrolyte hydrogels possess both ions and ion transport channels to replicate this kind of electricity generation behavior. When the polyelectrolyte is fixed (crosslinked) in the hydrogel, only the ionized ions can move freely [36–40]. By controlling the directional movement of free ions, electrical power can be generated, which is the basis for the design and preparation of self-powered hydrogel sensors [41].

In this work, as a proof of concept, the common anionic electrolyte polyacrylic acid (PAA) is used as backbone to assemble a highly elastic PAA covalent hydrogel as a platform for mechanical-electrical conversion and sensing. Based on theoretical simulations and experimental results, we observe that the local ion concentrations inside the elastic polyelectrolyte hydrogel can vary due to the change of its internal structure by external mechanical force, thereby completing the conversion of mechanical energy into electricity and accompanying the mechanical signal recognition. The self-powered response capability of the sensor is proven to be adjustable, which is closely related to the contact area, strain, and pressure. Manipulating the direction of free ion transport allows the sensor to easily recognize where the pressure is applied. Lastly, the self-powered hydrogel exhibits more accurate sound detection capabilities than traditional resistive sensors. Overall, this simple and low-cost flexible device based on polyelectrolyte hydrogel is promising for applications in self-powered sensing and energy harvesting.

2. Results and discussion

2.1. Design principle of self-powered polyelectrolyte hydrogels

In a salt solution, both cations and anions move randomly. When electric power is applied, the ions will move directionally to realize the electric conduction of the circuit [42]. If the anions and cations in the solution spontaneously move in opposite directions, the movement of electrons occurs in the external circuit connecting the two different directions [43,44]. In addition, due to the concentration gradient, ionizable salt in the high-concentration region will autonomously diffuse to the low-concentration region. When an ion-selective membrane is used between the two regions, the movement of one type of ion (cation or anion) can be restricted and the directional diffusion of the oppositely charged ion can be obtained (Fig. 1a). This will also induce the movement of electrons when connected to an external circuit. The internal 3D hole of the hydrogel can be used as a channel for ion transmission to achieve a similar power generation effect (Fig. 1b) [37,45].

It is known that polyelectrolytes can ionize movable ions when water is present, but since polyelectrolyte chain acts as a hydrogel skeleton, it is restricted from free movement. We assume that the compression of the anion polyelectrolyte hydrogel will increase the local (TOP of hydrogel) polymer concentration, which will cause the directional diffusion of free ions (+) inside the hydrogel and consequently, the movement of electrons in the external circuit (the polyelectrolyte chains cannot move freely and thus cannot offset the net displacement of cation). This reveals that the polyelectrolyte hydrogel has the ability to convert mechanical energy to electricity (Fig. 1c). When the elastic network of the hydrogel recovers, the generated dynamic electrical signals (output voltage or current) will gradually disappear (Fig. 1d). This hypothesis also supports the idea that polyelectrolyte hydrogel can realize self-powered pressure/strain sensing while achieving mechanical energy-electricity conversion [46]. In this work, we follow the electric-generating model based on ion concentration gradient-induced ion-directed motion in hydrogels [43,44,47–50]. However, while this work was under revision, a new interpretation has been proposed [41]. Our results are compatible with both models. Currently, the mechanism is still under debate.

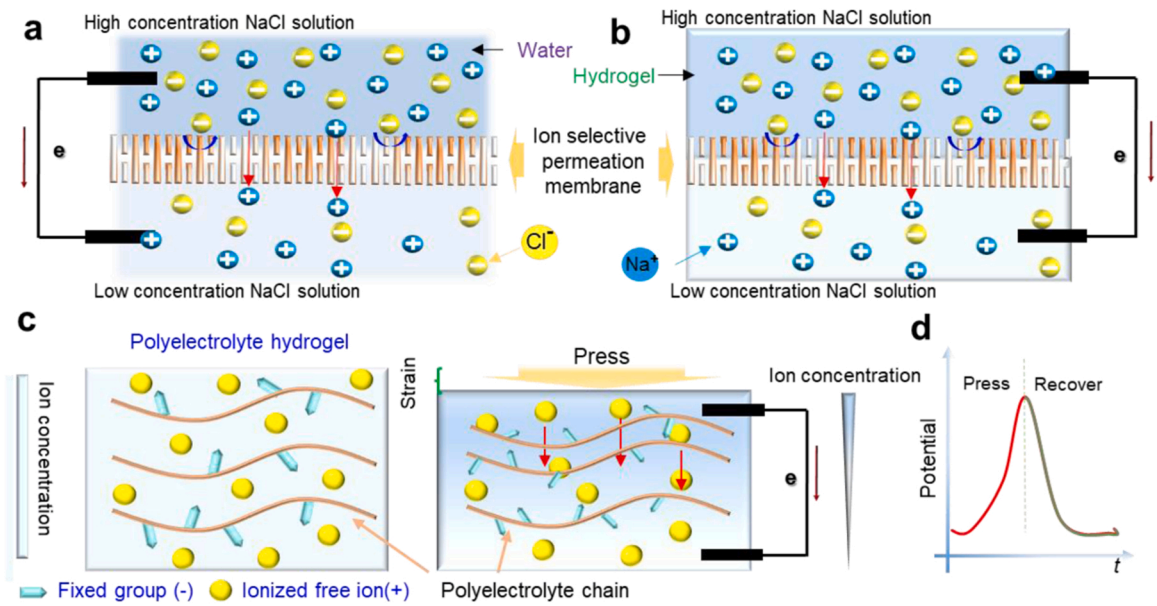

Fig. 1. a) Schematic diagram of electric-generation caused by the diffusion of high-concentration salt (NaCl) solution to low-concentration salt solution through ion selective permeation membrane. b) Schematic diagram of electric-generation caused by the diffusion of hydrogel with high-concentration salt (NaCl) to hydrogel with low-concentration salt (NaCl) through ion selective permeation membrane. c) During the compression process, the anion polyelectrolyte hydrogel will have uneven distribution of ion concentration and subsequent diffusion, resulting in the conversion of mechanical energy into electricity. d) After the elastic network of hydrogel is restored, the ion concentration will be restored uniformly, and the hydrogel completes self-powered strain sensing.

Herein, the typical anionic polyelectrolyte PAA hydrogel was prepared as a research model. This hydrogel is formed by covalently cross-linking PAA chains. Both acrylic acid (AA) monomer and PAA hydrogel are negatively charged (Fig. S1). Therefore, ionized PAA by deprotonation of the -COOH groups can provide the conductivity of the hydrogel (Fig. S2). Fig. 2a reveals a model diagram of a mechanical-electric converter assembled from a cylindrical PAA hydrogel (d=2.5 cm) combined with soft electrodes of graphite paper. According to Fig. 2b, when the hydrogel is gradually compressed from the top with a press, its output voltage will increase rapidly. At a 50 % compressive strain, the pressure and strain are held steady, the relative output voltage and current of the hydrogel also remain stable (~6 mV and ~ 2 μA, Fig. S3). These results demonstrate that the compression deformation of polyelectrolyte PAA hydrogel can be converted into electrical signals linearly. In particular, when the compression deformation of the hydrogel is maintained, the output signals are steady, which basically satisfies two of the three elements of strain/pressure sensing, that is, response and stability [10,51,52].

The above results are consistent with our original hypothesis. The compression behavior of the PAA hydrogel may lead to a gradual decrease in the compression degree (relative displacement) from the top to the bottom, so that the H^+ concentration gradually decreases from the upper to bottom surfaces of the hydrogel (Fig. 2b). Thanks to the H^+ concentration gradient, H^+ in the hydrogel will diffuse downward to generate an output voltage. The net charge displacement of H^+ and the PAA chains (-) caused by the compression process is zero, that is, the downward compression process does not generate electrical power. The power generation of the hydrogel stems entirely from the diffusion of H^+, which can also be proven by the result that the output voltage of hydrogel remains stable (not disappeared or significantly reduced) while maintaining compressive strain (50 %).

The positive or negative movements of H^+ will increase or decrease the output voltage, which gradually decreases during reverse compression (Fig. 2c), presenting strong evidence of the reverse movement of H^+ (Fig. 2d). The two processes are almost symmetrical. Therefore, it can be concluded that the directed diffusion of H^+ underpins power generation. According to thermodynamic equilibrium, the output potential (ΔU) of PAA hydrogel can be described as

$$\Delta U = \frac{RT}{qF} ln \frac{C(H)}{C(L)}$$

where R, T, q, and F are the gas constant, temperature, valence, and Faraday's constant respectively. In addition, $C(H)$ and $C(L)$ represent the H^+ concentration on the high-concentration side and the low-concentration side of the hydrogel surface, respectively [47–49]. The detailed derivation can be found in the Supplementary information. This formula indicates that the intensity of the induced voltage (output voltage) is directly related to the concentration gradient of H^+, which in turn, is determined by the degree of compression (strain or force).

We further studied the local H^+ concentration of PAA hydrogel because of compression. As presented in Fig. 2e, in reference to the original hydrogel, the compressed polymer network of PAA hydrogel (50 % strain) will be denser. Also, the increase in the conductivity of the hydrogel caused by compression can prove that the compression deformation will cause the enhancement in the local H^+ concentration in the hydrogel system (Fig. S4). In addition, finite element method (FEM) simulation was used to analyze the local displacement and polymer mesh distribution of the columnar uniform hydrogel structure under various compressive strains (Fig. 2f). The simulation results proved that compression of the hydrogel will cause the difference in displacement or deformation of the hydrogel from top to bottom. As the compressive strain increases, the difference in compression of the polymer grids on the upper and lower surfaces of the gel gradually becomes larger. This also implies that the compression causes the H^+ concentration difference between the upper and lower surfaces of the gel to gradually increase. The operating mechanism of PAA hydrogels that convert mechanical energy into electricity is attributed to the H^+

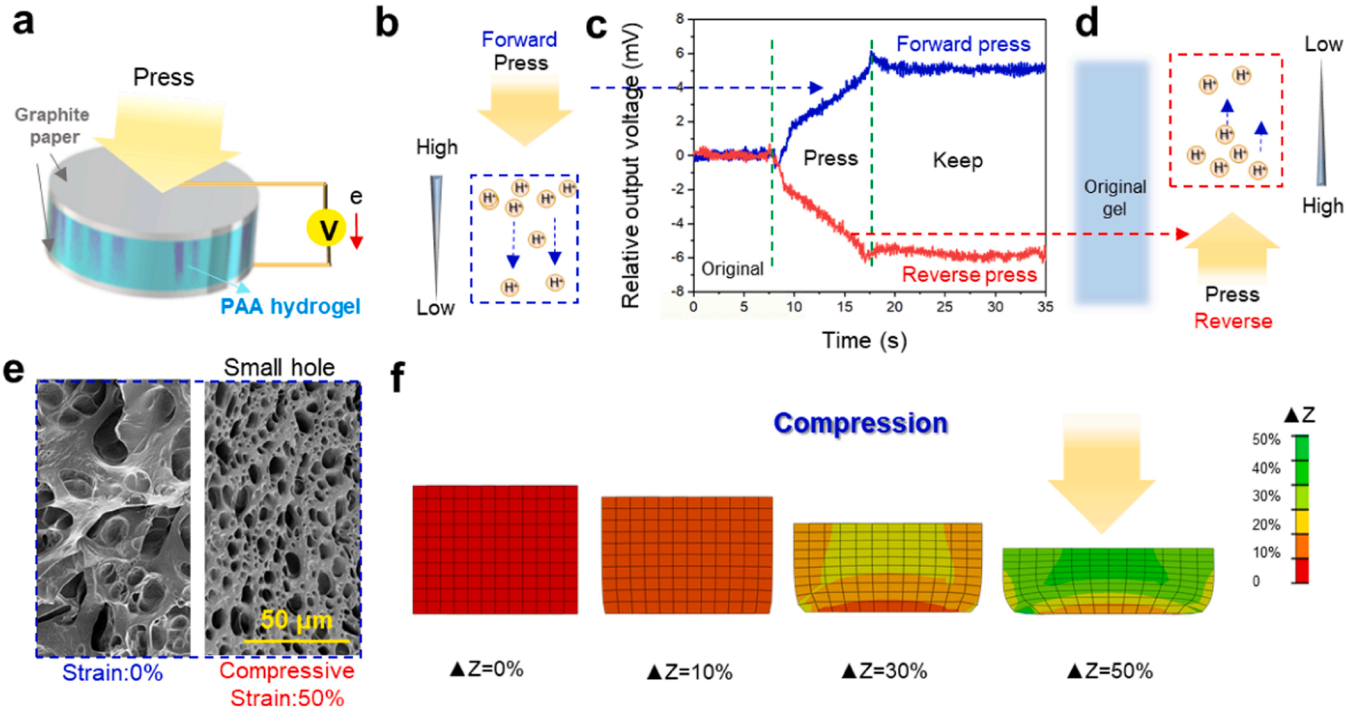

Fig. 2. a) Schematic diagram of PAA hydrogel-based mechanical-electric conversion model. b) The working principle of PAA hydrogel converting mechanical energy into electrical energy during forward compression. c) The relative output voltage (pulse) of PAA hydrogel changes in response to external dynamic compression behavior. d) The working principle of PAA hydrogel converting mechanical energy into electricity during reverse compression. e) SEM images of the internal structure of PAA hydrogels under various compressive strains. f) Finite element simulation of local displacement distribution and PAA network state of hydrogels under different compressive strains (ΔZ represents displacement).

concentration difference of the hydrogel caused by external compression, which triggers the directional diffusion of H^+, ultimately generating electricity.

2.2. The self-powered sensing performance of polyelectrolyte hydrogels

As mentioned, the PAA hydrogel satisfies the two fundamental elements of strain/pressure sensors: response and stability. More importantly, high elasticity is essential for proper operation of the hydrogel-based pressure/strain sensor, allowing a full recovery of the initial shape and thus of the electronic signal [53]. In this work, we studied the signal recovery and stability of PAA hydrogel-based sensors. As shown in Fig. 3a and b, the hydrogel exhibited almost identical response (~6 mV), drop curve, and programmed recognition time (~7 s) to four independent reciprocating mechanical compressions (strain: 50 %). The stable compressive stress-strain curves confirm the elastic recovery and stability of the hydrogel, which is critical for a pressure/strain sensor (Fig. 3c). Moreover, compression speeds of 10, 50, 100 and 200 mm/min were applied to test the output voltage of the PAA hydrogel (strain: 50 %). The results show that the output voltage is only related to the degree of compression (pressure or strain), but not directly related to the speed of compression (Fig. S5). The maximum detection limit of the PAA gel device collected here is ~5 N, while the minimum detection limit is ~0.05–0.1 N (Fig. S6; the results are derived from the analysis of Figs. 2c and 3c).

When the hydrogel gradually recovers, the H^+ concentration difference at the corresponding position will decrease, causing the output voltage to drop until it reaches zero. These results indicate that polyelectrolyte PAA hydrogel has all the characteristics of self-powered pressure/strain sensing. The signal output of the hydrogel also has been proved to be adjustable. The output voltage/current can improve by increasing the strain/pressure amplitude (strain) or increasing the contact area (Figs. 3d and S7). Based on the adjustability of the output signals, the hydrogel can recognize and respond to various strains and pressures, thereby expanding its possible applications. To further confirm the stability of the external pressure sensing mechanism, the hydrogel was compressed by applying strain for multiple cycles from 0 % to 10 %. We found that a stable response voltage pulse to the same strain (10 %) within 1000 s can be maintained (Fig. 3e).

2.3. The self-powered sensing application of hydrogels

We have shown that polyelectrolyte hydrogels have direction-dependent self-powered sensing capabilities. Based on this feature, a self-powered orientation (position) recognition sensor was developed. As presented in Fig. 4a, the sensor is composed of a PAA hydrogel and two graphite paper electrodes. It is possible to split this device into three regions from left to right, A, O and B (the left and right electrodes of the hydrogel recognizer need to be connected to the negative and positive electrodes of the test instrument respectively). When pressing different areas of the sensor, distinct output signals can be generated. As shown in Fig. 4b, when part A is pressed, the output voltage increases rapidly. This is because the H^+ concentration in part A increases as a result of the compression, which subsequently causes H^+ to diffuse to the right side. On the other hand, when part B is compressed, the output voltage of the sensor decreases rapidly, which is caused by the H^+ of B part movement to the left side. Interestingly, when part O is pressed, no relative output voltage from the hydrogel sensor is generated. This is because, at the part O (the center of the hydrogel detector) the net H^+ displacement is close to zero (the left and right diffusion are the same, with opposite direction). In addition, we performed controlled experiments to consider the possible thermoelectric and triboelectric interferences caused by finger pressing on the gel. These results support the hypothesis of mechanic-electric conversion of the gel, where the electricity is not derived from thermoelectricity, piezoelectricity, and triboelectricity (Fig. S8 and Movie S1) [54–58].

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Importantly, traditional resistive sensors exhibit nondirectional response to pressing (Fig. S9) [59]. This is due to the difference in the

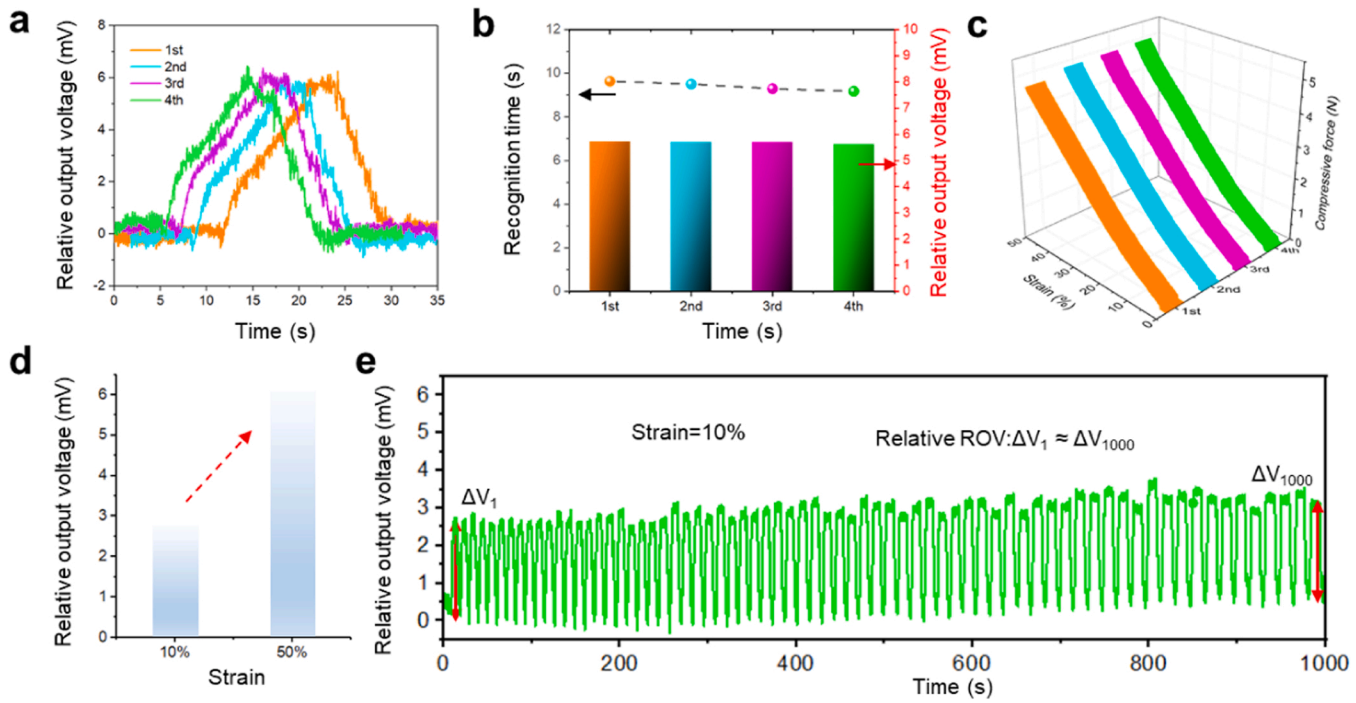

Fig. 3. a) The relative output voltage changes in response to the four-independent compression (strain:50 %)-recovery processes of the PAA hydrogel. b) The recognition time and response amplitude of hydrogel to compressive strain (50 %). c) Four- independent compression force-strain curves of hydrogel. d) The relative output voltage changes (pulse) in response to the various compressive strain of the PAA hydrogel. e) The self-powered strain response stability of PAA hydrogel (strain:10 %).

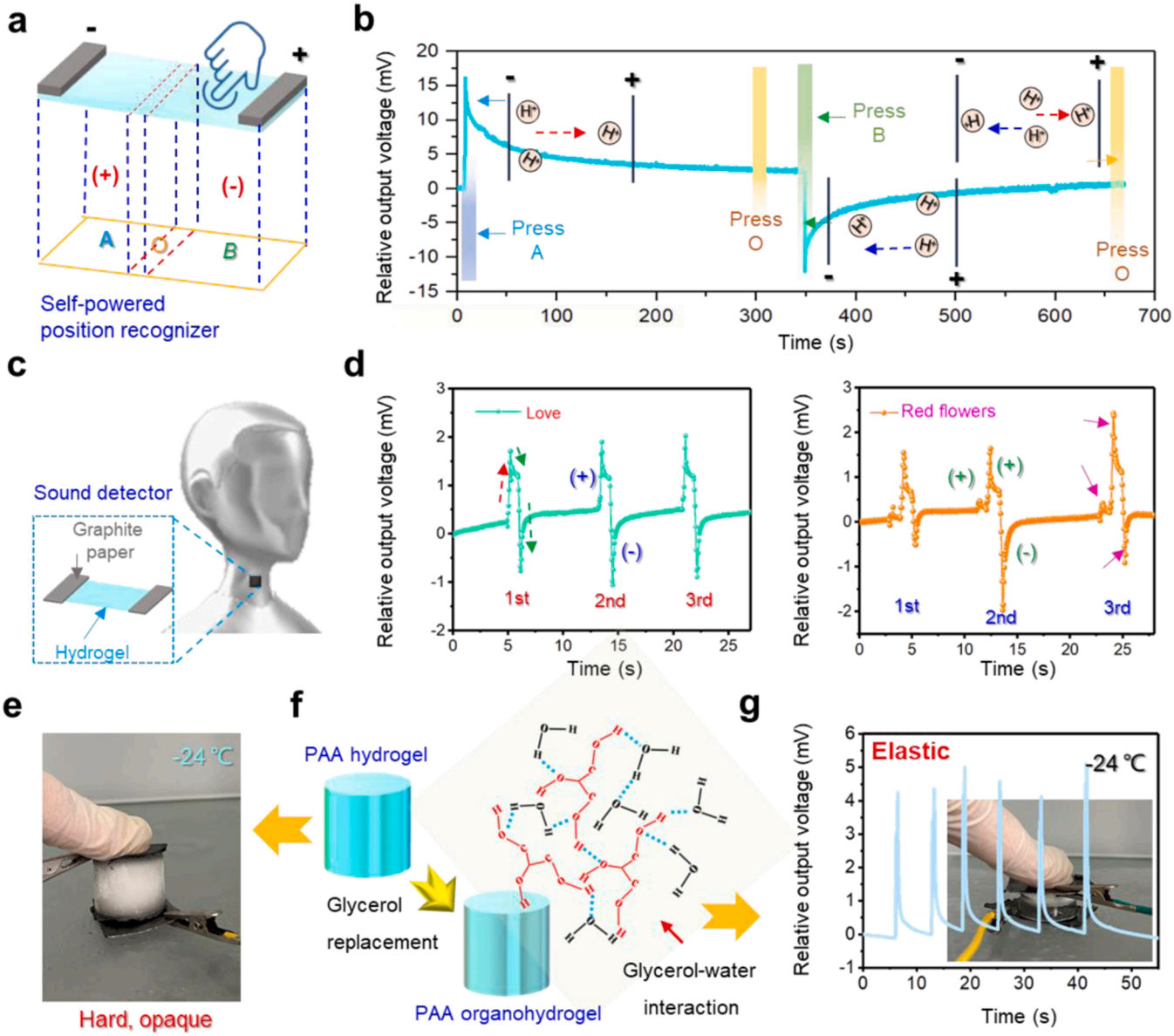

Fig. 4. a) Application diagram of self-powered position recognizer. b) The relative output voltage changes of detector in response to pressing of different positions of the recognizer. c) Schematic diagram of the PAA hydrogel-based sound detector. d) The relative output voltage changes of detector in response to various sounding letters "love" and "red flowers". e) The original PAA hydrogel will freeze at −24 ° and lose its elasticity. f) PAA hydrogel undergoes glycerol solvent replacement to obtain PAA organohydrogel. g) PAA organohydrogel can realize self-powered sensing at low temperature (−24 ℃).

response mechanism from the direction-dependent self-powered sensing that is being developed in the present study. The external mechanical compression can change (increase or decrease) the resistivity, but in this type of device the pressing position cannot be easily detected.

In contrast, the as-obtained direction-dependent self-powered PAA hydrogel sensor can not only complete the recognition of position and direction to operate like a switch, but also serve as self-powered voice recognizer. Fig. 4c presents a wearable and self-powered sound detector based on the PAA hydrogel. When a person wearing this detector pronounced particular words, such as "love" or "red flowers", repeatable and distinguished curves of electric signal were measured (Fig. 4d). Compared to traditional resistive sensor-based sound monitors, the self-powered hydrogel exhibits multi-dimensional response characteristics that are very helpful for improving the accuracy of sound recognition (Fig. S10).

Generally, hydrogel-based devices suffer from freezing at ultra-low temperatures (Fig. 4e). However, PAA hydrogel can be readily imparted with antifreeze capability by simple solvent replacement, obtaining antifreeze PAA organo-hydrogel (Figs. 4f and S11) [60,61]. The latter can realize stable self-powered sensing also in sub-zero temperature environments (Fig. 4g). Moreover, the obtained PAA organo-hydrogel proved a long-lasting solvent retention that increases the service life (Fig. S12) [62]. Overall, PAA hydrogel possesses favorable characteristics for the design and application of a wide range of environmentally adaptable self-powered sensors.

2.4. *The mechanical energy collection of various polyelectrolyte hydrogels*

Importantly, PAA hydrogel exhibits excellent processability and potential for large-scale production. For example, a large-size transparent PAA hydrogel (300 cm^2) can be prepared (Fig. 5a). PAA hydrogels also have excellent customization capabilities: as demonstrated in Fig. 5b, an insole incorporating a cropped PAA hydrogel-based device is fabricated. This insole can be placed in any pair of shoes to collect the

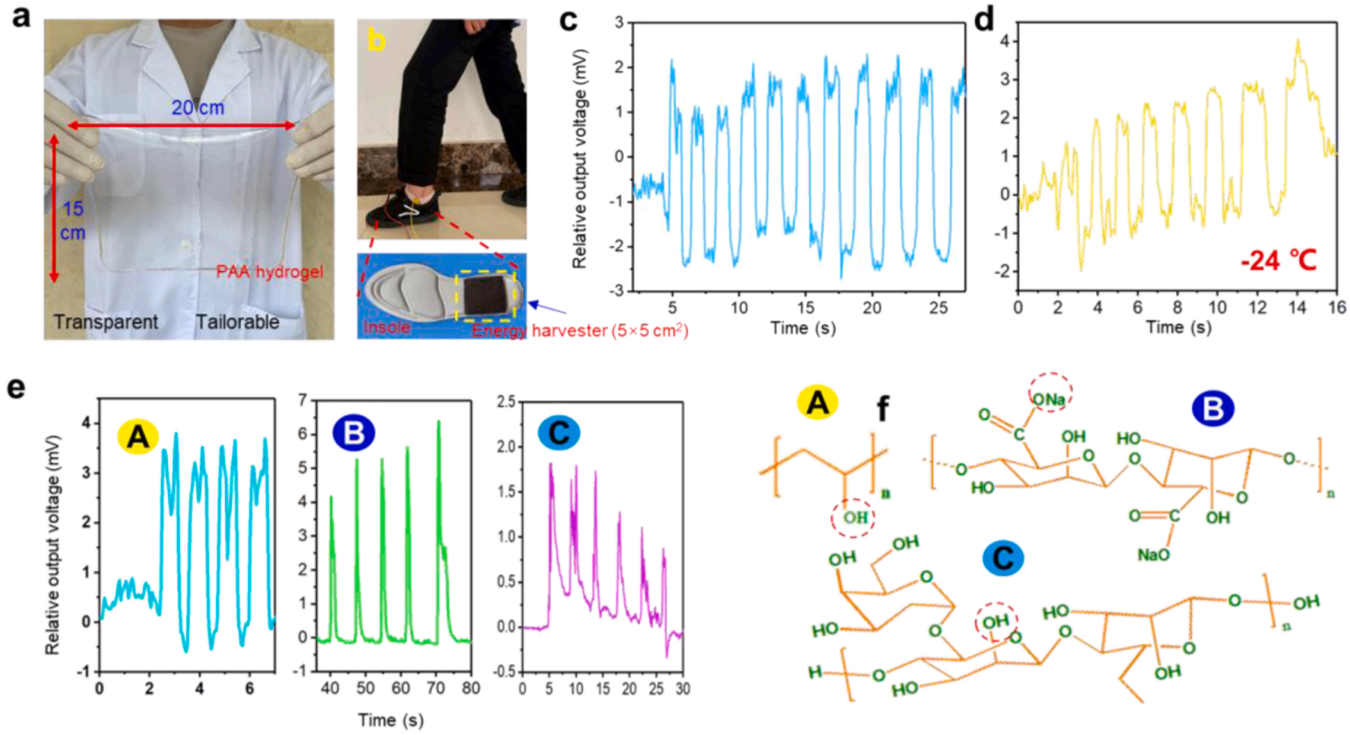

Fig. 5. a) PAA hydrogels hold great transparency and are tailorable. b) The energy harvesting insole assembled by PAA hydrogel and graphite papers(electrode) can be used for mechanical energy harvesting. c) The relative output voltage of the new insole containing PAA hydrogel changes in response to the dynamic walking behavior of human. d) The relative output voltage of the new insole containing PAA organohydrogel changes in response to the dynamic walking behavior of human. e) The mechanical energy harvesting result of various polyelectrolyte hydrogels. f) The chemical structure of different polyelectrolytes, A: polyvinyl alcohol; B: sodium alginate; C: guar gum.

mechanical energy generated by human motion. The new insole can effectively convert the mechanical energy associated with the leg's continuing movement to electricity (Fig. 5c). Since the hydrogel is not completely uniform, a small initial voltage output may already exist. Therefore, only the pulse (relative voltage output) that converts mechanical energy into electricity was recorded. Similarly, PAA organohydrogel, which has been replaced with glycerol, can also be used for mechanical energy collection at temperatures below zero (−24 °C, Fig. 5d). Although the electrical output from the new insole may be small, this type of polyelectrolyte PAA hydrogel-based energy harvester is simple and low-cost. Thus, as a new type of mechanical energy collection device, its potential in the continuous collection of daily walking energy can still be substantial. The concept discussed is also universally applicable to many hydrogels containing polyelectrolytes. In fact, like PAA hydrogels, other polyelectrolyte hydrogels, such as polyvinyl alcohol (PVA), guar gum, and sodium alginate hydrogels, can convert mechanical energy into electricity (Figs. 5e, f, and S13).

3. Conclusions and perspectives

We designed and fabricated a polyelectrolyte PAA hydrogel inspired by salinity-gradient power generation, which can realize mechanical energy conversion and self-powered sensing. By combining simulations and experimental results, we propose an interpretation of the mechanical energy-to-electricity conversion mechanism of PAA hydrogels, which is derived from the directional H^+ diffusion induced by compression deformation. Taking full advantage of the unique self-powered sensing principle, we have developed both PAA hydrogel-based self-powered position recognizers and multi-dimensional sound detectors. Importantly, the mechanical-to-electric energy conversion concept is rather universal, and applies to various polyelectrolyte hydrogels. This mechanical-electric conversion device has large comprehensive advantages compared to common hydrogel-based piezoelectric and triboelectric electronics (Table S1). This simple and low-cost flexible device based on polyelectrolyte hydrogels is promising for several emerging technologies, including self-power sensing and energy harvesting.

CRediT authorship contribution statement

X.P. and Q.W performed all the experiments; X.P. and Q.W. wrote the first draft; X.P and D.B. discussed the data and revised the manuscript D. B., Y.N. and F.R. supervised the work; all authors participated in editing the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.107718.

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