

Giant Iontronic Flexoelectricity in Soft Hydrogels Induced by Tunable Biomimetic Ion Polarization

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Flexoelectricity features the strain gradient-induced mechanoelectric conversion using materials not limited by their crystalline symmetry, but state-of-the-art flexoelectric materials exhibit very small flexoelectric coefficients and are too brittle to withstand large deformations. Here, inspired by the ion polarization in living organisms, this paper reports the giant iontronic flexoelectricity of soft hydrogels where the ion polarization is attributed to the different transfer rates of cations and anions under bending deformations. The flexoelectricity is found to be easily regulated by the types of anion-cation pairs and polymer networks in the hydrogel. A polyacrylamide hydrogel with 1 M NaCl achieves a record-high flexoelectric coefficient of \approx 1160 μ C m⁻¹, which can even be improved to \approx 2340 μ C m⁻¹ by synergizing with the effects of ion pairs and extra polycation chains. Furthermore, the hydrogel as flexoelectric materials can withstand larger bending deformations to obtain higher polarization charges owing to its intrinsic low modulus and high elasticity. A soft flexoelectric sensor is then demonstrated for object recognition by robotic hands. The findings greatly broaden the flexoelectricity to soft, biomimetic, and biocompatible materials and applications.

gradient induced by nonuniform deformation such as bending or flexing.^[1] Compared to piezoelectricity, flexoelectricity is not limited by materials' crystalline symmetry, and exists in many kinds of materials including ceramics,^[2] dielectric polymers,^[1c,3] liquid crystals,^[4] semiconductors,^[5] and even biomaterials.^[6] Owing to the wide materials choices, multifunctional flexoelectric transducers are potentially designed to fit various applications in smart sensors,^[7] actuators,^[8] and power generators.^[9] Nevertheless, the flexoelectric polarization is still too low for many practical applications. According to Kogan's model,^[10] the flexoelectric coefficient is expressed as $\mu_{iikl} =$ $P_i / \frac{\partial \epsilon_{jk}}{\partial x_l}$, where P_i and $\frac{\partial \epsilon_{jk}}{\partial x_l}$ are the electric polarization vector and strain gradient tensor, respectively. Therefore, high flexoelectric coefficient and high strain gradient are essential for large polarization. However, state-of-the-art flexoelectric materials either are too brittle to withstand

1. Introduction

Flexoelectricity describes a mechanoelectric conversion effect that the electric polarization is linearly coupled with strain large bending deformations^[11] or exhibit very small flexoelectric coefficients^[12] (Table S1, Supporting Information).

Unlike the electric polarization mechanism of flexoelectric or piezoelectric solid crystalline materials, living organisms

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Figure 1. Scheme of the biomimetic ion polarization in hydrogel. a) The transmembrane ion polarization generates action potentials as the mechanoreceptors in the human skin response to the pressure stimuli. b) Schematic illustration of generated flexoelectric voltage by a bent hydrogel sandwiched between two flexible Ag/AgCl electrodes. c) (i) Schematic diagram of the gradient distribution of internal strain in a bent hydrogel, (ii) schematic illustration of the ion polarization in the hydrogel under strain gradient, attributed to the faster displacement rate of the blue anions than that of the red cations from the compressed to the stretched region, (iii) COMSOL simulation of the pore pressure of the bent hydrogel, and (iv) COMSOL simulation of electric potential in the hydrogel under bending deformation.

generate electricity based on ion polarization or ionic current for sensing and communicating.^[13] For example, soft mechanoreceptors sense external stimuli due to the mechanically gated generation of action potentials through the transmembrane ion polarization (Figure 1a).^[14] Recently, increasing interests have been devoted to developing iontronic mechanisms analogous to biological systems, which are oriented to the great potentials in human-interfaced or biomedical applications.^[15] Particularly, piezoionic effect has been found that nonuniform mechanical compression (such as indentation) can induce net ion current and ion polarization in soft hydrogels with either polyelectrolyte or neutral polymer networks.^[15a,16] Flexoelectricity has also been reported using ionic polymer electrolyte membranes (PEM),^[17] where strain gradient-induced ion polarization is attributed to the opposite transport of different-sized cations and anions of ionic liquids. The iontronic flexoelectricity allows the use of soft materials, achieves much higher flexoelectric coefficients, and therefore is highly promising for developing various mechanoelectric transducers.

In this work, we examine the soft hydrogel as a flexoelectric material and report the record-high iontronic flexoelectric coefficient. Ion polarization in hydrogel can be generated when dissolved cations and anions displace from the compressed region to stretched region along with the water at different rates under bending deformations (Figure 1c). This process produces unbalanced cation/anion distribution and a net ion flux through the hydrogel, outputting finally the electrical signals in external circuits, accordant with the recently investigated piezoionic effect in soft hydrogels.^[15a] The exploration of hydrogels as flexoelectric materials brings the following great advantages: i) first, giant flexoelectricity can be achieved. The flexoelectric coefficient of the polyacrylamide (PAM) hydrogel swollen with 1 м NaCl solutions was measured to be 1160 $\mu C \ m^{-1}$ at 0.5 Hz bending deformation, which is orders of magnitude higher than other reported flexoelectric materials. Thanks further to the intrinsic softness of hydrogel (low modulus and high elasticity), high flexo-polarization charge density was obtained at very large deformation gradients. ii) Second, the flexoelectricity of the hydrogel can be easily tuned

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by the polymer matrix networks (e.g., polycation or polyanion hydrogel) and/or the types of dissolved ions (e.g., different chloride salts). iii) Third, the flexoelectric hydrogel allows potentially the biocompatible applications where current toxic PEMs are not applicable. Herein, we demonstrated the application using the selfpowered flexoelectric sensors for robotic hand to distinguish different grabbed objects.

2. Results and Discussion

2.1. The Flexoelectricity of the PAM Hydrogel

To explore the flexoelectricity of the hydrogel, we constructed the device with a sandwich structure, where a PAM hydrogel swollen with 1 м NaCl aqueous solution was sealed between two flexible Ag/AgCl electrodes (see details in the Experimental Section), as shown in Figure 1b. Once the PAM hydrogel is bent to a certain curvature (the mechanical loading mode being shown in Figure S1 and discussed in Text S1, Supporting Information), the strain gradient is formed along the thickness direction in the cross-section of the PAM hydrogel, that the inner layer of the neutrosphere is compressed and the out-layer is stretched (Figure 1c(i) and Figure S2, Supporting Information). Then, water and ions are forced to produce convection through the pores of the hydrogel, moving from the compressed region to the stretched region along the pore pressure gradient. The net negative ionic current inside the hydrogel is generated due to the faster migration rate of chloride anions than that of sodium cations, and similar conclusions have been demonstrated as the piezoionic effect in previous articles.^[15a] This process breaks the statistical neutrality of the hydrogel, forms ion concentration gradients and therefore produces ion polarization, generating in turn a potential difference between the two electrodes to balance the internal ion polarization field, as depicted in Figure 1c(ii). Similar mechano-ionic effect has been documented earlier in polyelectrolyte hydrogel as streaming potential caused by the flux of single-sign mobile ions,^[18] and recently has further been perfectly verified to exist in hydrogel with neutral polymer networks but cations and anions diffusing at different rates.[15a]

We utilized finite element simulation by COMSOL Multiphysics to simulate the voltage generation process in hydrogels under bending deformation. As detailed in Text S2 (Supporting Information), the poroelastic mechanics were coupled with Poisson-Nernst-Planck equations to derive the transient distribution of pore pressure [Figure 1c(iii)], ion concentration (Figure S3, Supporting Information) and electric potential [Figure 1c(iv)] inside the hydrogel under bending deformation. It is confirmed that the bending deformation can lead to the high pore pressure in the inner layer while low pore pressure in the out-layer of the curved hydrogel. Therefore, the water and ions migrate along the pore pressure gradient according to the Darcy's law. Due to the different migration rate of ions, the fast-migration anions could be concentrated in the outer layer, which then ultimately develop the electrical potential difference between the out-layer and inner layer. Note that, for the electrostatic calculations, a very distant sphere outside the hydrogel was added as a grounding point and the air was used to fill the ball. Also, the two end areas were not covered by electrodes for the following experimental tests. The

dynamic evolution of the pore pressure, anion concentration, and electrical potential is shown in Movie S1–S3 (Supporting Information), respectively.

The open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) were recorded at different bending curvatures and frequencies. The curvatures were controlled by the displacement along the loading direction (along x-axis in Figure S1, Supporting Information). As the two pristine electrodes were not perfectly in equilibrium, there was always an offset background current and voltage, which has been commonly observed in many reported iontronic devices.^[15g,19] The variation of the electrical signals reflects the iontronic flexoelectricity. Note that the reference electrode of the testing instrument Keithley 6517 was ground to a metal plate, while the top electrode was always connected as a counter electrode and the bottom electrode was treated as the working electrode (Figure S4, Supporting Information). When bending the hydrogel, $V_{\rm oc}$ is positive (subtracting the background signal), consistent with the reasoning that the deformation gradientinduced net Cl⁻ anion flux inside the hydrogel is from the bottom to the top; meantime, the I_{sc} in external circuits balancing ion flux in hydrogel is positive when bending and negative when releasing (Figure 2a). It is emphasized that the polarity of $V_{\rm oc}$ and I_{sc} is reversed if the bending deformation is upside-down, also confirming the mechanism hypothesis (Figure 2a). Furthermore, it is observed that the electrical outputs increase with the increased bending curvatures (see photos of bending curvatures in Figure S5 and corresponding outputs in Figure S6, Supporting Information); whereas, the higher bending frequency leads to the lower electrical outputs (Figure 2a). At a fixed curvature of 187.6 m⁻¹, the peak-to-peak V_{oc} and I_{sc} can be 1.49 mV and 76.53 µA at 0.5 Hz frequency, which decrease to 0.92 mV and 17.22 µA at 2 Hz frequency, respectively. As for a counterpart uniform compression deformation, the electric outputs are orders of magnitude lower (Figure S7, Supporting Information), confirming the deformation-gradient induced electricity-generation mechanism. The curvature- and frequency-dependent flexoelectricity trend is consistent with previous flexoelectric PEMs.[17]

The flexoelectric coefficient (μ) of the hydrogel was then evaluated (Figure 2b). The amount of ion polarization charges (P) can be calculated by the equation: P = Q/A, where charge quantity Q is the integrated area of a current peak induced by flexion and A is the sample area. The flexoelectric coefficient can be simplified to a scalar form as the ratio between the ion polarization charges (P) and strain gradient $\left(\frac{\partial \varepsilon}{\partial z}\right)$, i.e., $\mu = P/\frac{\partial \varepsilon}{\partial z}$. The strain gradient is simplified as the curvature of the neutrosphere at the bending center of the hydrogel (see Text S3 and Figure S2, Supporting Information). The obtained flexoelectric coefficient is 1160, 309, and 57 $\mu C~m^{-1}$ at 0.5, 1 and 2 Hz frequency, respectively. If comparing the flexoelectric coefficient at the same frequency with that in literature, it is found that the hydrogel shows the record-high coefficient among all reported flexoelectric materials, which is several orders of magnitude higher than ceramics,^[1b,d,2b,11b] dielectric polymers,^[20] liquid crystals,^[4] and biomaterials,^[6,21] and is also about an order of magnitude higher than the PEMs^[17] (Figure 2c). By optimizing the polymer networks, the flexoelectric coefficient can be even improved to 2340 μ C m⁻¹ at 0.5 Hz (see discussions below). The comprehensive comparisons are listed in Table S1 (Sup-







Figure 2. The iontronic flexoelectricity in the PAM hydrogel with 1 NaCl. a) Output electrical signals of the hydrogel being bent at different frequencies but the same curvatures (187.6 m⁻¹). The insets illustrate the loading mode and bending directions. b) The flexoelectric coefficient of the PAM hydrogel at different frequencies. c) Comparison of the flexoelectric coefficient and Young's modulus of the PAM hydrogel with other reported materials.^[1b,d,2b,4,6,11b,17,20,21] d) Comparison of the maximum pressure gradient and polarization charge density of the PAM hydrogel with other reported materials.^[1,2b,3,4c,11a,12b,17b,c,22,23]

porting Information). Another advantage of the hydrogel is its low Young's modulus (39.47 kPa, as seen in Figure S8, Supporting Information), which is about the lowest among all synthetic flexoelectric materials and is close to the in vivo biomaterials. Due to the intrinsic softness of the hydrogel, it can withstand much larger deformation and therefore obtain orders of magnitude larger polarization charges, which is especially a big advantage over reported rigid ceramic,^[1a,b,d,2b,11a] dielectric polymer materials,^[1c,3,12b] liquid crystals,^[4c,22] and PEMs.^[17b,c,23] As seen in Figure 2d and Table S1 (Supporting Information), the polarization charges (169.3 mC m⁻²) and tested curvatures (187.6 m⁻¹) both are record-high as well. Therefore, it can be expected that the flexoelectricity of hydrogel could be possibly of great significance in wearable and implantable applications when large deformation, high polarization charge, and excellent biocompatibility are required.

2.2. The Effect of Different Cation Species on Flexoelectricity

Then, the effect of different cation–anion pairs in hydrogels was investigated to further support the proposed mechanism and also to optimize the iontronic flexoelectricity. The flexoelectricity of PAM hydrogels with two different chloride salts and hydrochloric acid but same concentration (1 M) was compared, i.e., KCl, NaCl, and HCl. It is observed that the outputs of hydrogel containing NaCl and KCl have the same polarity, but the former one shows larger electrical outputs; whereas, the electrical polarity of hydrogel containing HCl is reversed and the output amplitudes are also the highest (**Figure 3**a). We interpreted these trends based on the model proposed by Madden et al.,^[15a] where the flow in hydrogel is treated in transition state and the difference in ion–polymer network interactions is vital for electricity generation. Under pressure gradient, the movement of ions is balanced by



Figure 3. The effect of the cation species on the flexoelectricity. a) The electrical outputs of the PAM hydrogel swollen with 1 μ KCl, 1 μ NaCl, and 1 μ HCl being bent at the same curvature (310.4 m⁻¹) and frequency (2 Hz), respectively. b) The illustration of the correspondingly different ionic polarization induced by these three hydrogels. c) The peak-to-peak voltage and current produced by the hydrogel with varying polymer content under the same testing condition. d) The stability of the flexoelectric outputs under prolonged cycling tests.

the dragging force from water molecules and hindering force from the polymer pores, therefore the speed of cations (v_+) and anions (v_-) can be written as (see details in Text S4, Supporting Information):

$$\nu_{+} = \frac{D_{+}}{D_{0+}} \nu_{+} \nu_{-} = \frac{D_{-}}{D_{0-}} \nu \tag{1}$$

where D_{0+} or D_{0-} is the diffusion coefficient of the cations or anions in bulk aqueous solution, respectively; D_+ or D_- is the diffusion coefficient of the cations or anions in the hydrogel, respectively; and ν is the water flow rate, following Darcy's law. Then, the short-circuit current density (j_s) and open-circuit electric potential (ΔV) can be derived as^[15a]

$$j_s = -\frac{en\kappa}{\eta} \left(\frac{D_+}{D_{0+}} - \frac{D_-}{D_{0-}} \right) \nabla p \tag{2}$$

$$\Delta V = -\frac{enk}{\sigma\eta} \left(\frac{D_+}{D_{0+}} - \frac{D_-}{D_{0-}} \right) \Delta p \tag{3}$$

where *e* is the electronic charge, ∇p is the pressure gradient, *n* is the concentration, κ is the permeability, η is the viscosity, and σ is the conductivity of the hydrogel. Obviously, there will be no electricity, if the cations and anions transfer at the same rate or the polymer matrix has equal hindering effect on the cation and anions. In bulk aqueous solution, the diffusivity of the involved

ions follows the sequence that $H^+ > Cl^- > K^+ > Na^+$. Based on our data, we could conclude that, in PAM hydrogel, the hindering effect of polymer matrix to these ions follows about the sequence that $H^+ < Cl^- < K^+ < Na^+$, so that the transfer rate difference of Cl⁻-to-Na⁺ is larger than Cl⁻-to-K⁺ and the reversed H⁺-to-Cl⁻ rate difference causes the opposite polarity of ion polarization (Figure 3b). Coincidentally, the transfer rate sequence of the involved ions is similar to that in the bulk aqueous solutions; but, in the flexoelectric hydrogel, the transfer rate difference could root from more complicated reasons, such as the size difference of solvated ions and the different hindrance effect on the ions by the polymer networks.^[24] Meantime, the electrical outputs are found to increase with the NaCl concentration (Figure S9, Supporting Information), which is accordant with above equations. Furthermore, it can therefore be explained that the increased polymer content in the hydrogel enhances the hindering or filtering effect to the ions,^[25] leading to the improved ion polarization and electrical outputs (Figure 3c). It is noted that the hydrogel with 25% polymer content was chosen for testing other than specifically mentioned, because that the sample with 50% or more polymer content showed lowered elasticity (Figure S8, Supporting Information) and could not withstand prolonged severe bending cycles. As for the hydrogel with 25% polymer content, the flexoelectric outputs show no significant degradation after 7500 cycles of bending tests, confirming the excellent durability (Figure 3d). In addition, the short-circuit current was also measured for the hydrogel containing 1 M Na₂SO₄ (Figure S10, Supporting Information). It is observed that the electricity polarity was reversed comparing with that containing 1 M NaCl, consistent with the proposed mechanism.

2.3. The Effect of Polyelectrolyte Chains on Flexoelectricity

Based on the above model, we further regulated the ion-polymer network interplay to optimize the flexoelectricity by designing double-network hydrogels containing either polycation or polyanion chains. As shown in Figure 4a(i), the poly(diallyl dimethyl ammonium chloride) (PDAC) as the polycation networks was added to the PAM hydrogel (PDAC-PAM hydrogel). Even if there is no other salt dissolved in the hydrogel, a $V_{\rm oc}$ of about 2.44 mV and peak-to-peak I_{sc} of about 20.13 µA can be obtained at a bending curvature of about 310.4 m^{-1} and frequency of 2 Hz (Figure 4b). In PDAC, the Cl⁻ anions can be dissociated by water molecules, leaving the PDAC chain positively charged. Since only the anions are freely moveable, the bending deformation will result in the net anion flux along with the water flow. This ionic current generation phenomenon is consistent with previously reported streaming potential.^[18,19] Then, after adding extra NaCl into the PDAC-PAM hydrogel, the electrical outputs at the same test conditions increases, and increasing NaCl concentration can further improve the outputs (Figure 4c). With 2 M NaCl, the V_{0c} and peak-to-peak Isc raise to about 4.15 mV and 80.87 µA, respectively. Therefore, the enhancement effect on the polarization is confirmed because the ion polarization polarity of bare polycation hydrogel is coincident with that induced by Cl⁻-to-Na⁺ diffusivity difference [as schemed in Figure 4a(ii)]. However, if 1 м HCl is added in the PDAC-PAM hydrogel, the polarity of the electrical outputs can be reversed (Figure 4b). As schemed in Figure 4a(iii), the opposite polarity of the H⁺-to-Cl⁻ diffusivity difference will weaken or even reverse the original ion polarization of polycation hydrogel (Text **S5**, Supporting Information).

Similar trends were also found in polyanion hydrogels. We designed further a double-network hydrogel (PSSNa-PAM hydrogel) containing polyanions [poly(styrene sulfonic acid) sodium salt, PSSNa] chains and PAM chains. Unlike the PDAC, the freely mobile ions in PSSNa are sodium cations, balanced by the anions fixed in the backbone of the polymer. Therefore, the Na⁺ cations will be collected at the stretched side of the PSSNa-PAM hydrogel under the bending strain gradient, which induces net cation flux and the ion polarization with polarity contrary to that of bare PDAC-PAM hydrogel [see the scheme in Figure 4d(i) and electrical outputs in Figure 4e]. Accordingly, adding NaCl into the hydrogel can weaken or reverse the ion polarization and electrical outputs because Cl- anions at higher transfer rate were included [Figure 4d(ii)]; whereas, adding HCl can enhance the ion polarization and electrical outputs due to the introduced extra net H⁺ cation flux [Figure 4d(iii)]. As for the former case, it is fortunate that the NaCl concentration can be easily tuned, and the crossover of the two effects can be observed. As seen in Figure 4f, increasing the NaCl concentration reduces the voltage amplitude, and the polarity of voltage is reversed when the concentration is over about 1 м (Figure 4f). Besides, the ionic conductivity of the PSSNa-PAM hydrogel increases with the NaCl concentration (Figure S11, Supporting Information). This trend confirms that the added NaCl weakens the streaming effect in polyanion hydrogel and, at certain high concentration, the Cl⁻ anion flux overwhelms the Na⁺ flux. As for the latter case with extra HCl, there are three different types of mobile ions, i.e., H⁺, Na⁺, and Cl⁻, and the voltage should be estimated as (Text S5, Supporting Information)

$$\Delta V = \left\{ -\frac{en_4}{\sigma \eta} \frac{D_{Na^+}}{D_{0Na^+}} - \frac{en_6k}{\sigma \eta} \left(\frac{D_{H^+}}{D_{0H^+}} - \frac{D_{Cl^-}}{D_{0Cl^-}} \right) \right\} \Delta p$$
(4)

where n_6 is the concentration of added HCl and n_4 is the concentration of Na⁺ dissociated from the PSSNa chains. The enhancement of the voltage is because that the term $(\frac{D_{H^+}}{D_{0H^+}} - \frac{D_{Cl^-}}{D_{0Cl^-}})$ is positive and therefore additive to the electric potential generated by pristine net sodium ion transfer alone. Based on above discussion, it is suggested that the PDAC-PAM hydrogel with extra 2 \bowtie NaCl is promising to achieve improved flexoelectric coefficient. Therefore, it was tested under different bending curvatures under the frequency of 0.5 Hz (Figure S12, Supporting Information). The obtained flexoelectric coefficient reaches 2340 μ C m⁻¹ at 0.5 Hz.

2.4. The Soft Flexoelectric Sensor for Object Recognition

Considering the high flexoelectricity of the hydrogel under bending deformation, a soft self-powered sensor for bending angle detection was designed and applied in robotic hand for object recognition. The $V_{\rm oc}$ of the hydrogel sensor was tested under different bending angle (θ), which was defined as the angle between the horizontal direction and the top surface of the device (Figure 5a and Figure S13, Supporting Information). The V_{oc} increases with the bending angles, and the gauge factor (determined as $dV/d\theta$) is calculated to be 0.02 mV $^{\circ-1}$ when the angle is below 50°, and 0.04 mV $^{\circ-1}$ in the range of 50°–75°. It is noted that the sensor can distinguish the upward and downward bending, as the polarity of ion polarization and therefore the voltage output is opposite when the bending direction is reversed (Figure 5b). Compared with other resistive sensors,^[26] our flexoelectric sensor is self-powered as it can directly output voltage signals without power source; furthermore, it can distinguish the bending direction through the voltage polarity. The sensor was then applied to monitor the movement of a wrist. The opposite voltage signals are generated when the wrist is bent in two different directions (Figure 5c), indicating that it is sensitive to the bending direction as well. When tested in air without encapsulation, the water in the hydrogel evaporates, causing the malfunction of the sensor. Appropriate encapsulation using polydimethylsiloxane (PDMS) can keep the electrical output of the sensor unchanged for 10 d, which can partially solve this issue for practical applications (Figure S14, Supporting Information). We then applied the sensor in a robotic hand for object recognition with the aid of machine learning (Figure 5d). Five sensors can be well fitted at the finger joints of a robotic hand to record the movement of every finger. As shown in Figure 5e, different sets of electrical signals can be obtained through the multichannel acquisition system (Figure S16, Supporting Information) when different objects are grasped by the manipulator, such as tennis balls, Rubik's cubes, cylindrical water bottles, cups, and funnels. The machine learning algorithm was used to analyze the obtained electrical signals to improve

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Figure 4. The effect of polyelectrolyte hydrogels on the flexoelectricity. a) Schematic illustration of the ion polarization under the strain gradient in the PAM-PDAC hydrogel (double-network hydrogel with polycation PDAC chains) with no extra salt (i), $1 \le NaCl$ (ii), and $1 \le HCl$ (iii), respectively. b) The open-circuit voltage and short-circuit current of three PAM-PDAC hydrogels bending at the same curvature ($310.4 \ m^{-1}$) and frequency (2 Hz). c) The outputs of PAM-PDAC hydrogel with varying NaCl concentrations. d) Schematic illustration of the ion polarization under the same strain gradient in the PAM-PSSNa hydrogel (double-network hydrogel with polyanion PSSNa chains) with no extra salt (i), $1 \le NaCl$ (ii) and $1 \le HCl$ (iii), respectively. e) The corresponding flexoelectric outputs. f) The variation of flexoelectric outputs with the NaCl concentrations.

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Figure 5. Self-powered soft bending sensor. a) Summarized voltage-bending angle variation of the sensor. b) The voltage generated by the sensor being bent in two different directions at the same angle of 45°. The insets are photos of the hydrogel being bent in different directions (scale bar: 5 mm). c) The detection of wrist motion (scale bar: 4 cm). d) Schematic illustration of the application using this sensor for robotic object recognition with the aid of machine learning. e) The electrical signals of five sensors attached on a robotic hand grabbing different objects like tennis ball, Rubik's cube, cylindrical water bottle, cylindrical cup, and funnel (scale bar: 5 cm). f) The machine learning process of the training and test verification. g) Cluster results of the sensor (Label "0-4" referring to the robotic hand grabbing tennis ball, Rubik's cube, cylindrical water bottle, cylindrical cup and funnel, respectively). h) The classification confusion matrix with the overall accuracy of 99% (Label "0-4" referring to the robotic hand grabbing tennis ball, Rubik's cube, cylindrical water bottle, cylindrical cup and funnel, respectively).

the recognition accuracy. Each of five sensors at the finger joints recorded 100 sets of data when the robotic hand grasped the same object. Then, all the data of these sensors capturing different objects were analyzed by a support vector machine (SVM)-based software platform as the training set, as schemed in Figure 5f.

Another 20 sets of data generated by each of five sensors, obtained at five different hand gestures, were collected as test data to justify the training result. The resulting *t*-distributed stochastic neighbor embedding (t-SNE) shows clearly the features from five different classes (labeled as "0-4" referring to the robotic hand grabbing tennis ball, Rubik's cube, cylindrical water bottle, cylindrical cup and funnel, respectively) (Figure 5g). The confusion matrix with validation accuracy of 99% is achieved as shown in Figure 5h, demonstrating further the excellent object recognition capability.

3. Conclusion

In conclusion, we reported the giant flexoelectricity of soft hydrogels is attributed to the ion polarization which is caused by the difference in transfer rates of cations and anions under strain gradient of bending deformations. Record-high flexoelectric coefficient was obtained for PAM hydrogel swollen with 1 м NaCl, reaching 1160 µC m⁻¹ at 0.5 Hz. Furthermore, it was found that the flexoelectricity, both the polarity and magnitude, can be regulated by the polymer chain networks and cation-anion pairs in the hydrogel. The ion polarization caused by the streaming effect of polyelectrolyte hydrogel and that induced by cation-anion diffusivity difference can be additive when their polarities are the same, or subtractive when their polarities are the opposite. By optimization, the PDAC-PAM hydrogel containing 2 м NaCl enhanced flexoelectric coefficient to 2340 µC m⁻¹ at 0.5 Hz. Other advantages of the hydrogel as flexoelectric materials include its intrinsic softness to withstand large deformation gradient and excellent biocompatibility. Finally, a self-powered flexoelectric angle sensor was demonstrated for object recognition. In the future, it is interesting to investigate the coupling between mechanoionic effects with other ionic electricity-generation mechanisms such as temperature gradient-based thermocells.^[27]

4. Experimental Section

Materials: Herein, sodium chloride (NaCl), acrylamide (AAM), N,N'-methylenebisacrylamide (MBAA), ammonium persulfate (AP), and N,N,N',N'-tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich. Potassium chloride (KCl), hydrogen chloride (HCl), potassium metabisulfite (Ag₂S₂O₅), sodium sulfate (Na₂SO₄), sodium polystyrenesulfonate (PSSNa), and poly(diallyl dimethyl ammonium chloride) (PDAC) were purchased from Aladdin. Sodium hyposulfite (Na₂S₂O₃), silver nitrate (AgNO₃), potassium metabisulfite (K₂S₂O₅), ammonium acetate (CH₃COONH₄), and aminothiourea (CH₅N₃S) were purchased from Macklin. The stretchable conductive textile was purchased as the elastomer.

Preparation of Stretchable Ag/AgCl Electrode: The soft and flexible Ag/AgCl electrode was prepared by an electroplating process.^[28] The purchased conductive textile was washed in the alcohol for 10 min in the ultrasonic machine, and then was washed in the water for 5 min. The cleaned cloth was blow-dried with an air gun. The plating solution required for silver electroplating process was prepared. 30 g L^{-1} AgNO₃ and 40 g L^{-1} $K_2S_2O_5$ were, respectively, added to a quarter of the total volume of water. 225 g L^{-1} Na₂S₂O₃ was dissolved in the water with a third of the total solution volume. Then the K₂S₂O₅ water solution was joined to the AgNO₃ solution, which would form white precipitates in the water. The whole cloudy solution was poured into the $Na_2S_2O_3$ water solution. 25 g L⁻¹ CH₃COONH₄ was added in the final solution and a certain time should be waited. CH₅N₃S should be added in the solution to keep the PH value of 5.5-6.0. The 99.9 wt% pure silver plate was used as anode and the conductive textile was the cathode. The current density and electroplating duration were 0.25 A dm^{-2} and 20 min, respectively.

The Ag/AgCl electrode was obtained by electroplating the Ag-coated cloth.^[29] Platinum foil was used as the counter electrode, and the Ag-

coated cloth was the working electrode. The two electrodes were immersed in the 0.1 μ HCl solution. The DC powder of 0.6 V for 10 min was applied for the electroplating process. Finally, the Ag/AgCl electrode was quickly washed by the water and blow-dried.

Preparation of the Hydrogel: 1.6 g AAM, 0.01 g MBAA, and 0.05 g AP were completely dissolved in 10 mL water. NaCl, KCl, HCl, and Na₂SO₄ were added in the solution above, respectively. The PSSNa-PAM hydrogel was formed by adding 60 wt% PSSNa compared to the PAM to the prepolymerized solution. The PDAC-PAM hydrogel was prepared by adding the same weight PDAC to the pre-polymerized solution.

Preparation of the Device: The Ag/AgCl electrodes were cut to suitable shape and then put in the rectangular mold ($30 \text{ mm} \times 8 \text{ mm} \times 4 \text{ mm}$). The solution was also poured in the mold and would be cured within 10 min by the catalyst (TEMED). The whole device was obtained, and the Ag/AgCl electrode was in close contact with the hydrogel. The PDMS film (the ratio of Sylgard 184 and curing agent is 10:1 by weight) was obtained by spincoating at first, then cured at 60 °C for 3 h. The encapsulation process is that the entire device is packaged with PDMS.

Characterization and Measurement: A step motor (LinMot E1100) was applied to make the device bend at the continuous oscillations. The maximum speed and frequency for the test were 1 m s⁻¹ and 2 Hz, respectively. Besides, the output electrical signals were measured by an electrometer Keithley 6517. The test machine (YL-S71, Yuelian, China) was applied to test the Young's modulus of the hydrogel. The electrochemical workstation (CH1760E) was used as the DC power to electroplate the Ag and AgCl and was applied to test the impedance of the hydrogel with different amounts of NaCl.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

biomimetic, flexoelectricity, iontronic, sensor, soft hydrogel

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