Adaptive Deformation of Ionic Domains in Hydrogel Enforcing Dielectric Coupling for Sensitive Response to Mechanical Stretching

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Understanding the role of ionic migration in salt-doped hydrogels is crucial for designing and using ionic skins. This study systematically investigates a typical ionic skin in the aspects of variations in capacitance and conductance with respect to stretch ratio. The ionic skin exhibits a sensitive response to the stretch ratio and input frequency. The capacitance can increase by 145% with increasing stretch ratio, whereas the ratio of capacitance variation to stretch ratio can exceed 0.25. The capacitance decreases with increasing frequency, whereas conductance increases. Capacitance or conductance with respect to stretch ratio exhibits an inflection point when the input frequency is fixed. Herein, an ionic domain model is proposed in which the ionic domains deform adaptively with global strain and released active ions. A portion of movable ions strengthens dielectric coupling, thereby significantly enhancing capacitance, and some of them act as free ion channels to increase conductance. The dielectric coupling is weakened when the active ions arriving at the electrode are depleted by either a significantly high frequency or large strain. This study will be useful for signal handling in ionic skin with high flux and high sensitivity and may also assist in understanding computing and memory principles of biological bodies.

1. Introduction

Artificial skin can be used on human bodies or robots and has become a widely discussed issue in the fields of artificial intelligence, flexible electronics, and materials science.[1] Although various types of artificial skins have been proposed,[2] there are extreme difficulties in simulating real skin. The skin feels subtle forces and heat stimuli and then identifies the magnitude and mode of each with very high spatial and temporal resolution. Its structure provides these beneficial properties.[2c,3] The skin has large amounts and types of sensor molecules, which are capable of coding and encoding signals and can also transfer tactile signals to neurons. Its matrix consists of macromolecules containing salt solutions. The ions in the matrix of the real skin are reasonable signal carriers but have far more complex functions. The salt content and type of solution significantly influence signal generation and transfer. In addition, the skin can undergo large deformations and recover to a relaxed state. These features, such as sensor molecules, are difficult to fabricate, and synthetic molecules with similar structures cannot be integrated into artificial skin to extract the evoked signals. However, using salt-doped hydrogels as the matrix for ionic skin is a promising approach, as these hydrogels are similar in composition and density to real skin, as well as sharing many of its physical and chemical properties.[2b,4] Such structures have great ductility and can detect various deformation strains, including bending and stretching, by measuring the modification in capacitance and conduction.[2b]

Numerous studies have focused on extending the field of ionic skin.[2c-5] Regarding key hydrogel materials, most studies have focused on enhancing ductility, to provide high sensitivity to certain types of mechanical touch, provide self-healing capabilities, etc.[6] However, few studies have provided detailed discussions on how a signal is generated and transferred in salt-doped hydrogels. Obtaining strong responses based on the specific desired

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type of input and output modes is a major trend in current research. For example, some studies have focused on achieving high conductance and have therefore used salt-doped hydrogels as an ionic conductor and cable.[7] Very high electrical voltages (≈kV), which are impractical for human applications, are loaded on such materials to conduct electrical signals. Some studies extract conductance signals, whereas others use capacitance signals.[3b,8] Occasionally, high-frequency stimulation is used; however, low-frequency or even direct current (DC) input can also be used.[2b,6c] Therefore, general recognition and standards involving signal modes are required. The interrelationships between the signals and deformations are not clear. A complete understanding of the working mechanism of either the skin or the hydrogel has not been reported thus far, and the candidates studied to date function appropriately only in limited modes and environments.[8a] Although empirical formulas have been obtained, their physical origins are unknown.[9] Different matrix materials should be integrated to handle different types of stimuli and deformations, which may prove difficult. The candidates studied also differ from real skin because the latter can respond to various types of stimuli based on a single matrix. The electronic signals induced by either deformation or heat conduction typically comprise a linear zone and a nonlinear zone, which depend on changes within the deep structures and the stimulation modes. Generally, the linear zone is used for convenient signal handling. However, the nonlinear zones are physiologically and physically significant and should not be neglected.

In this study, a salt-doped hydrogel-based ionic skin structure of a particular type (Figure 1a) was selected to examine the interrelationships among capacitance, conductance, and stretch ratio to exploit the principle of ionic migration during input and deformation. Both capacitance and conductance were found to increase sensitively with the stretch ratio up to a critical value and decrease afterward. The capacitance decreases as the conductance increases with increasing input frequency. Based on the experimental results, we treated the salt-doped hydrogel as a plasma-like system at room temperature and proposed an ionic domain model for microscopy. It was found that ions are released adaptively from the ionic domains under the stretching process and can be re-established at the electrode interface to enforce dielectric coupling. This characteristic can reasonably explain the sensitive and smart responses to various types of mechanical stimulation. Our study will also be helpful for understanding signal generation, transmission, memorization, coding, and encoding in a biological entity.

2. Results and Discussion

A bending experiment was performed with the ionic skin secured to a finger (Figure 1b). The capacitance and conductance were recorded during the bending process through Cu tape electrodes connected to an impedance analyzer. The participant bent his finger as close to the required angle as possible. During bending, the voltage was swept from −3 to 3 V and the frequency was maintained at 1 MHz. The fixed amplitude and frequency bending results are plotted in Figure S1, Supporting Information. As shown in Figure 1c, the capacitance and conductance increased abruptly and synchronously when the finger was bent, which is consistent with reported results.[2b] The capacitance increased by 38.5% and the conductance by 113%. The ratio between these two enhanced amplitudes was ≈0.34 for the same deformation. The variations in capacitance and conductance with deformation are significantly different from those of conventional dielectric ceramics and related composites. The macroscopic strain under external force is normally very small for conventional dielectric ceramics; therefore, the capacitance and the proportional conductance do not vary with deformation. If a major strain occurs, resulting in a large number of defects and even cracks, the measured capacitance will drop because of the dielectric loss, and the conductance will increase as a result of increased leakage along the dangling bonds. Ceramic composites can solve the deformation problem. However, the resistance increases with the stretch ratio.[10] Thus, the ionization of either the doped salt or water in the samples contributes to the increased capacitance and conductance during the deformation, as shown in Figure 1.

To establish the effects of salt doping and water as well as to determine the quantitative interrelationships among deformation, capacitance, and conductance, we stretched the samples and simultaneously tested their capacitance and conductance. Stretching was performed using a home-made microstretcher with a minimum displacement of 0.01 mm and a force of 0.135 N. The force–stretch ratio curve for sample E is shown in Figure S2, Supporting Information. Figure 2 indicates that initially, the conductance increases significantly for the samples containing hydrogel, prior to stretching (Figure 2a). The residual water in the hydrogel (samples B and C) should provide conductive protons, partially from those present already in the body and partially from ionization because of the high-frequency inputs. Salt doping significantly enhances the capacitance or dielectricity. The salt-doped samples have high dielectricity and considerable conductance,
although these two parameters oppose each other in conventional inorganic ceramics. Second, the samples have good ductility and elasticity, as shown in Figure 2b,c. The maximum stretching ratio increased by a factor of seven. The samples could almost recover to the initial state after stress relaxation, as only a low hysteresis could be observed.

Third, the conductance changes linearly with the deformation of the VHB tape at a very low slope (see sample A), and the capacitance decreases with the stretch ratio, as reported in the literature. Stretching reduces the cross-sectional area in the strain zone and establishes the reason for the linear variability of conductance under deformation. Figure 2d,e show the ratios between the relative changes in capacitance and conductance. The large absolute value of this ratio for the VHB tape indicates that there is no charge compensation in the deformation area, resulting in a decrease in dielectricity. These results indicate that the VHB tape plays a minor role in the results of the hydrogel-containing samples. The results in Figure 1 also indicate that the ions in the hydrogel form an electrical double layer (EDL) near the electrode and induce electrode polarization (EP). The increase in capacitance contributed by the EDL or EP is far greater than the reduction in capacitance caused by the charge loss in the VHB tape.

Fourth, the variation trends of capacitance and conductance are quite different for the undoped and doped samples containing hydrogel. Both the capacitance and conductance decrease monotonically with the stretch ratio (λ) for the undoped samples, following a trend similar to that of the VHB tape. The difference is that the ratios of \( \frac{\delta C}{C_0} / \frac{\delta G}{G_0} \) are nearly constant for samples containing the undoped hydrogel. This indicates that the active protons contribute equally to both capacitance and conductance in the undoped samples. The number of active ions decreased during stretching, suggesting that no additional protons were present in the samples. In contrast, the capacitance and conductance of all salt-doped samples first increased with strain, but subsequently decreased after a critical stretch ratio was exceeded. The maximum value of \( \frac{\delta C}{C_0} \) was 145% at \( \lambda = 4 \) (Figure 2b). The dry (sample F) and the thinner hydrogel state (sample D) have relatively low capacitance inflection points, that is, \( \lambda = 2.5 \) to 2.8, whereas the thicker hydrogel state (sample E) has a relatively high capacitance inflection point, that is, \( \lambda = 4 \). The conductance variations exhibit similar trends, as shown in Figure 2c. The conductance can even be enhanced by approximately 14.4-fold. The inflection points for \( \frac{\delta G}{G_0} \) are higher than those for \( \frac{\delta C}{C_0} \) and are \( \approx 4.5 \) times higher for the dry and thinner hydrogel states (samples D and F). For the thicker hydrogel state (sample E), no inflection point is found within the testing range. The inflection points seem to occur as a result of hydrogel rupturing or cracking, and this is evaluated in the following analysis.

Fifth, the salt-doped samples were sensitive to stretching. The ratios of \( \frac{\delta (\delta C/C_0)}{\delta \lambda} \) were 0.25 to 0.28 for samples D, E, and F when \( \lambda < 3 \), so they can be treated as linear zones. The ratios of \( \frac{\delta (\delta G/G_0)}{\delta \lambda} \) are approximately 1 for samples D and F, but 0.5 for sample E, when \( \lambda < 3.5 \). The ratios of \( \frac{\delta C}{C_0} / \frac{\delta G}{G_0} \) depend on the sample state, type of deformation, and stretching velocity. They are estimated as 0.7 for the stretch ratio of 1.5, according to Figure 2e. This value is larger than that obtained in Figure 1d, indicating the different influences of bending and stretching. The ratios of \( \frac{\delta C}{C_0} / \frac{\delta G}{G_0} \) decreased with the stretching ratio of the salt-doped samples. This implies that the mechanism leading to the variation of capacitance (or dielectricity) becomes saturated more quickly.

Consequently, when there is no hydrogel or salt doping, the system responds to external strain in a negative mode, known as
depressive plasticity, as described in neuroscience. However, when the hydrogel is doped with salt, the responses are modified to a positive mode, known as potentiation plasticity. The bending experiments produced similar results regarding the response indicators, as did the stretching experiments. Because the ions in the hydrogel are movable, there will be a global undulation of the active ionic concentration. Local depletion or enrichment of ions weakens or strengthens the responses to external stimuli. Such variations are consistent with the physiological phenomena. The refractory period usually occurs after the depletion of ions, whereas the excitation is due to ionic injection. The nonlinear zones (or the zones around the inflection point) in the experimental curves have physiological counterparts.

Because the responses to external stimulation are modified intrinsically after salt doping, four groups of samples were selected to further examine the responses to stretch ratio and input frequency (as shown in Figure 3 and 4). The effects of salt doping were obtained by comparison with VHB tape results. It is shown that the capacitance of VHB tape decreased with an increase in the frequency, and its absolute value was significantly low. The $C-\lambda$ curves were only slightly affected by the frequency (Figure 3, blue panel). The measured conductance of the VHB tape increased with the frequency and varied with stretch ratio, as shown in Figure 2. The VHB tape results are consistent with those of typical dielectric materials. The absolute capacitance values of the salt-doped samples decreased with increasing frequency (Figure 3, black and red panels), whereas the conductance increased with increasing frequency (Figure 4, black and red panels). This indicates that higher frequency strengthens ionization but is not beneficial to ionic migration because an ion has a far larger mass than an electron. For the undoped sample containing the hydrogel, the protons are primarily provided by the residual ionized water molecules. The capacitance drops quickly after the frequency is increased above 100 kHz (Figure 3, green panels), which indicates that the ionization of the residual water reaches its saturation point above this frequency. The actual weight modifications of capacitance and conductance were approximately 120% and 146% at 1 kHz and $\lambda = 6$, respectively, for the sample immersed in 2.74 M NaCl solution (Figure 3 and 4, black panels). These results indicate that the dielectric signal can be amplified greatly at low frequencies because many ions migrate to the electrode to form a polarization layer. Although a high frequency is beneficial for conductance measurement, a high current density usually leads to local heating and increased energy consumption. Therefore, monitoring the dielectric signal may be an elementary method for evaluating biological body responses to external stimuli.

The variation trends in Figure 3 and 4 are consistent with the results shown in Figure 2 for the salt-doped samples. For the sample immersed in a 0.5 M salt solution (Figure 3 and 4, red panels), the inflection points of capacitance and conductance occurred at 100 kHz and $\lambda = 5.5$ and at 1 MHz and $\lambda = 2.5$, respectively. However, these values were higher for the sample immersed in a 2.74 M salt solution (Figure 3 and 4, black panels), i.e., inflection points occurred at 1 MHz and $\lambda = 3$ for the capacitance and at 1 MHz and $\lambda = 5$ for the conductance. Because the undoped sample contains ionized water, the capacitance and

![Figure 3. Capacitance variation with stretch ratio, input frequency, and salt concentration. The input amplitude was 0.5 V. The thickness of the hydrogel was 0.5 mm. The blue panels display the data for the VHB tape, whereas the others display those of samples containing hydrogels.](image-url)
conductance have similar inflection points as well (Figure 3 and 4, green panels). They are 1 kHz and $\lambda = 4.5$ for capacitance, and 10 kHz and $\lambda = 3$ for conductance, respectively. The reason for the nonvariation of the undoped samples with the stretch ratio in Figure 2 (samples B and C) is that the measuring frequency is significantly high ($f = 1$ MHz).

The nominal dielectric coefficients at 1 kHz (Figure 3 and 4) are $4.51, 5.5 \times 10^2, 6 \times 10^4,$ and $8 \times 10^4$ for the VHB tape, undoped sample, and salt-doped samples immersed in 0.5 and 2.74 M NaCl solution, respectively. The conductance values are $2.7 \times 10^{-9}, 6 \times 10^{-6}, 2.8 \times 10^{-5},$ and $4.7 \times 10^{-5}$ S, respectively. The measurements began at $10^7$ Hz and ended at 10 Hz. According to these data and results in Figure 3 and 4, newly activated ions are generated during the stretching process. The reason for the enhanced activation of ions is unknown and has not been clarified previously. These ions initially contribute toward the enhancement of both capacitance and conductance when the deformation is relatively small. However, ion depletions will occur once when the deformation strain is higher than the critical rate, depending on the salt and residual water content.

**Figure 5a** shows the $\lambda$-$f$ interrelationship at the inflection points for the sample immersed in a 2.74 M salt solution. This demonstrates that the critical strain at the inflection point decreases with increasing frequency. Because the critical stretching ratio is greater under low-frequency inputs, the inflection point or the nonlinear zone cannot be ascribed to ruptures or cracks in the hydrogel. Therefore, it must be induced by the variations in the number of ions arriving at the electrode interface. With a decrease in the frequency, more ions are present at the interface. Figure 5b compares the $\lambda$-$f$ curves at the inflection points between the doped and undoped samples. Apparently, the doped samples can accept a much higher input frequency and can extend the linear response zone. Based on the aforementioned results, a model is proposed for explaining why salt doping will enhance the dielectricity and conductivity and inflection points during stretching, among others.

Salt-doped macromolecules usually have a low number of active ions in ambient environments. We established a transport equation to describe ionic migration in a plasma-like system. This model successfully simulated the wave patterns and weight modifications of the pulse responses of salt-doped polyethylene oxide. Results indicate that strong stimulation will activate a large number of movable ions. Small clusters or domains will appear after impurities are doped into the electrolyte and hydrogel. The study of imogolite-poly(acrylic acid) hydrogels using small-angle X-ray scattering (SAXS) and small-angle neutron scattering demonstrates particle overlap, rotation, and deformation with external stretching, which depend on the imogolite concentration. Lithium salt doping can restructure polar groups in ionic liquids and promote alkyl chain domains. A system combining poly(2,2′-disulfonyl-4,4′-benedizide terephthalamide) (PBDT) and ionic liquid exhibits a very high nominal dielectric constant, similar to our system, which is ascribed to the cluster distribution of free ions. The PBDT rod bundle provides an increased plateau modulus. However, herein, the variations in all physical properties with deformation were not studied. Considering these structural similarities, we propose that plasma-like substance can also be used for describing the states of ions in the salt-doped hydrogel.
The ions aggregate in twisted macromolecule chains to form ionic domains, as shown in Figure 6a. The anions surround the domains to maintain charge neutrality. The ions embedded into the chains of semiconductor macromolecules help in mediating charges (or carriers) along the chains to enhance conductivity. For a hydrogel, the bandgap is much higher than that of the semiconductor; therefore, the hydrogel is an insulator. Salt doping brings ions into the hydrogel, thereby contributing to the conductance. Even for the hydrogel without salt-doping, the protons can also be conserved the twisted macromolecule chains. The difference is that the number of ions is much lower than that in the salt-doped hydrogel. In addition, the Debye length can be estimated if the ionic concentration in the hydrogel is equal to that of a totally ionized solution. The Debye length could be 2.9 or 6.9 μm for the sample immersed in 2.74 M salt solution, respectively. These values are one order higher than those evaluated for a binary electrolyte confined between blocking electrodes with dielectric layers. Thus, it may be more reasonable to consider the percolation-confining ionic pathway instead of only ionic concentration. The Debye length could also be evaluated according to the domain (or particle) size detected using SAXS. The size of the domain herein might be one order larger than that of the imogolite-doped hydrogel.

The ions on the surface of ionic domains can be easily driven to the electrode to form an EDL and enhance EP. Therefore, the measured capacitance and nominal dielectric coefficient are very high for the initial states of the ionic skin structure (Figure 1). This resembles a plasma system wherein the dielectric coefficient cannot be described as being in either a vacuum or in atmosphere. The capacitance changes depending on the system state in which the ionic distribution is modified. However, the VHB tape does not contain movable ions to hold the charge; therefore, its capacitance is determined only by its intrinsic polarization. Ionic migration enhances the leakage current (or charge); therefore, the measured conductance increases as well. The channel of this leakage current will be composed of free ions connected in series, which are not constrained in the ionic domains and do not approach the electrode. Thus, the enhancement of both capacitance and conductance is derived from the active ions, eliminating the constraint of the ionic domains. The former is due to the accumulated ions near the electrode, whereas the latter is due to the free ions in the matrix. This is the primary reason for the simultaneous enhancement of both capacitance and conductance in the initial state of the ionic skin structure.

The ionic domains can deform during the stretching process. They are elongated along the stretching direction, and their cross-sectional areas are reduced. The total surface area of the domains was enlarged. The ions in the inner parts of the domains migrate to the domain surface (as shown in Figure 6b). Therefore, the number of movable ions around the surface increases (as shown in Figure 6c), strengthening the EP considerably. Consecutive stretching leads to a system limitation: if the ionic domains are thin enough for all ions to be distributed along the domain surfaces, or the distance becomes longer, such that the ions cannot arrive at the electrode during the field-loading period, the number of movable ions will decrease, which weakens the EP. The schematics of the ionic skin are plotted in Figure 6d,e. Only one dimension along the stretching direction was considered. In the cross-sectional profile, for convenience, the ionic domains are plotted with an elliptical contour. The characteristic distance between the two domains was assumed to be D. The longer dimension of the elliptical domain is assumed to be the characteristic length r.

The initial objective of ionic conductor design is to identify a flexible and stretchable conductor. Enhancing its conductivity with respect to transfer signals as a metal cable is the primary goal. However, as shown in the aforementioned studies, both capacitance and conductance vary significantly and are sensitive to external deformation under very low voltage loading. The absolute values of conductance are very low. The signal transfer in the ionic system is completed through electrical coupling at the electrode interface. The current density in the matrix is very low. Using the aforementioned ionic skin system as a dielectric layer is favorable for both high sensitivity and reduced heat consumption. In addition, the conductance is positively related to the capacitance in a plasma system. Therefore, we first consider the capacitance in the structural model in Figure 6. According to the theory of dielectric elastomers, the capacitance for uniaxial stretching can be expressed as

\[
C = C_0 \lambda \quad (1)
\]

where \(C_0\) is the capacitance of the dielectric in the undeformed state, and \(\lambda\) is the stretch ratio. However, if the ionic skin

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**Figure 5.** Interrelationship between the stretch ratio (\(\lambda\)) and input frequency (\(f\)): a) Inflection points in the C-f and G-f curves for the sample immersed in 2.74 M salt solution. b) Inflection points for the undoped and doped samples.
structure in Figure 1 is considered as a series connection between two EDL layers and one dielectric layer,\(^{[2b]}\) the theoretical capacitance must be very small and compatible with the value of the VHB tape. The high initial value of capacitance cannot be reflected in Equation (1) because considerably high nominal dielectric constants are measured and obtained for the hydrogel layers directly connected to the external electrodes (see Figure S3, Supporting Information). The ionic skin is far from broken down under the added voltage. The charges coupling on either the electrode or the VHB tape are identical, and the capacitance calculated from such charges reflects the capacitance of the hydrogel. Therefore, the deformation-induced capacitance variation does not arise from the deformation of the VHB tapes, but rather from the intrinsic structural variation of the hydrogel. Equation (1) is also not suitable for the VHB tape because its capacitance decreases with the stretch ratio.\(^{[11]}\) Moreover, the nonlinear component of the \(C-\lambda\) curve is also neglected in Equation (2), and this is not due to the rupture of the hydrogel. Consequently, we consider that the capacitance and not the electrical field built in the VHB layer can be expressed as Equation (2), according to Figure 6d,e

\[
C = \frac{Q}{U} = \frac{1}{U} \sum_{i}^{N} \omega_i^C(S_i, D_i, f, \lambda)n_i(V_i, D_i, f, \lambda)
\]

where \(\lambda\) is the stretch ratio and \(f\) is the input frequency. They are all external variables loaded on the system. We assume that the linear density along the stretching direction is \(N\). The \(i\)th domain has \(n_i\) ions \((i = 1, ..., N)\), with volume \(V_i\) and surface area \(S_i\). The ion domains deform with stretching, so that the characteristic length of \(r_i\) and the characteristic distance of \(D_i\) shown in Figure 6 can vary in the stretching direction. Both \(V_i\) and \(S_i\) are functions of the parameter \(r_i\). The number of ions, that is, \(n_i\), in the individual domains should vary with \(V_i\) and \(r_i\). Some ions move away from the ionic domain during stretching. Some of them will arrive at the electrode interface to form an EDL and can be defined by \(\omega_i^C \times n_i\). The remainder will be free ions distributed along the stretching direction and can be defined by \(\omega_i^F \times n_i\). Accumulation \(\omega_i^C \times n_i\) determines the total ions contributing to the EDL or EP at the electrode interface. The ratio \(\omega_i^C\) should be a function of the surface areas \(S_i\) and \(D_i\) because the former stands for the capture cross-section, and the latter should be proportional to the distance to the electrode interface. All ions escaping from \(U\) are the external voltages kept constant during stretching. Equation (2) considers time \(t\) and stretching velocity \(d\lambda/dt\) to describe the kinetic process. Here, we adopt situations not explicitly containing time to describe the states in Figure 1 to 5, in which the measured results are extracted when the value of \(\lambda\) is fixed. The variation of capacitance with the stretch ratio \(\lambda\) can be expressed as

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**Figure 6.** Ionic domain model: a) Schematic of an ionic domain; b) Deformation of the ionic domain under stretching stress and ionic migration, c) redistribution of ions, d) initial distribution of ionic domains in ionic skin structure, and e) deformation of ionic domains and redistribution of ions under stretching stress.
The term \( \frac{dC_{s}}{d\lambda} \) is usually positive before stress concentration and cracking because the twisted molecule ring will be unwound during stretching. The term \( \frac{dC_{s}}{d\lambda} \) can be written as \( \frac{dC_{s}}{d\lambda} \) when both \( \frac{dC_{s}}{d\lambda} \) and \( \frac{dC_{s}}{d\lambda} \) are positive. The term \( \frac{dC_{s}}{d\lambda} \) must be negative because the elongated \( D_{l} \) will hinder the ionic migration contributing to EP.

The ions will leave the domain; however, the sign of \( \frac{dC_{s}}{d\lambda} \) depends on \( \frac{dV}{d\lambda} \). If \( \frac{dV}{d\lambda} \) is positive over a range of stretching ratios, then the term \( \frac{dC_{s}}{d\lambda} = \frac{dC_{s}}{d\lambda} \frac{dC_{s}}{d\lambda} \) will be positive. When the stretch ratio exceeds a critical value, \( \frac{dV}{d\lambda} \) decreases because a sufficient number of ions migrate and reduce the domain volume. The term \( \frac{dC_{s}}{d\lambda} \) will be negative because some ions will leave the domain when its environment is enlarged. A portion of the released ions will arrive at the electrode to form smaller domains and become free ions. Comparing these factors, we can expect that the variation in capacitance (C) with the stretch ratio (\( \lambda \)) should proceed from positive to negative with an inflection point in the C–\( \lambda \) curve, which is consistent with the results presented in Figure 2 and 3, indicating the depletion of movable ions.

The conductance is proportional to the capacitance of an ideal dielectric or plasma system, especially for an ideal parallel plate system without evident variations in plate area and distance. The conductance is also positively related to the capacity of the ionic skin system, according to the aforementioned results. This is consistent with the assumption of a plasma-like system. However, the inflection points of conductance always lag behind those of capacitance, as shown in Figure 3 and 4. Perculation should occur among the ionic domains if the doping concentration is significantly high. This situation leads to a fully proportional relationship between capacitance and conductance. Moreover, their inflection points relative to either the frequency or stretch ratio will be synchronous. However, the results in Figure 3 and 4 indicate that percolation does not occur. The absolute conductance values of the hydrogel were not high. Therefore, the contributions to conductance originate from two sources during and after stretching. The first source is the ions arriving at the electrode interface, and the second source is the free ions among the domains. The latter results in leakage current through the domains. The conductance can be expressed as

\[
G = G^{C} + G^{F} = \alpha C + \beta Q^{F} = \alpha C + \beta \sum_{i}^{N} \left( \frac{d\omega^{F}_{i}}{d\lambda} n_{i} + \omega^{F}_{i} \frac{dC_{i}}{d\lambda} \right)
\]

(6)

Here, \( \alpha \) and \( \beta \) are simply assumed to be linear coefficients that may depend on the ionic concentration. Thus, the conductance follows a similar trend varying with the stretch ratio; however, its cause is based on the leakage charges passing through free ions. The free ions released during deformation can be expressed as \( \sum_{i}^{N} \left( \frac{d\omega^{F}_{i}}{d\lambda} n_{i} + \omega^{F}_{i} \frac{dC_{i}}{d\lambda} \right) \). The first term \( \frac{d\omega^{F}_{i}}{d\lambda} \) should be positive because a portion of the released ions will remain in the matrix. In contrast, the term \( \omega^{F}_{i} \frac{dC_{i}}{d\lambda} \) should be negative because the ionic density in the ionic domains decreases with strain. Consequently, the G–\( \lambda \) curve exhibits an inflection point when the stretch ratio is sufficiently high to reduce the effective leakage path. In addition, the equation can qualitatively explain why the inflection point of conductance lags behind that of capacitance.

As ions typically exhibit considerably lower mobility than electrons, it is expected that the C–\( f \) curve varies with a contrasting trend, compared with the G–\( f \) curve, as shown in Figure 3 and 4. The frequency-induced movable ions arriving at the electrode can be expressed as \( \sum_{i}^{N} \left( \frac{d\omega^{F}_{i}}{d\lambda} n_{i} + \omega^{F}_{i} \frac{dC_{i}}{d\lambda} \right) \). The term \( \frac{d\omega^{F}_{i}}{d\lambda} \) must be negative because the number of ions arriving at the electrode decreases at high frequency. The term \( \omega^{F}_{i} \frac{dC_{i}}{d\lambda} \) is also negative because the ability to capture the free ions drops for the ionic domains at high frequencies. For conductance, this is reserved. According to the variation of free ions, that is, \( \sum_{i}^{N} \left( \frac{d\omega^{F}_{i}}{d\lambda} n_{i} + \omega^{F}_{i} \frac{dC_{i}}{d\lambda} \right) \), the term \( \frac{d\omega^{F}_{i}}{d\lambda} \) must be positive because more ions will either not arrive at the electrode or return to the ionic domains. Thus, the conductance does not increase monotonically with frequency after considering \( \frac{d\omega^{F}_{i}}{d\lambda} \) and \( \frac{dC_{i}}{d\lambda} \). Consequently, low-frequency input is more useful for capacitance measurement to obtain a large output, and high-frequency input is more suitable for conductance measurement.

The polymer domain has been proposed in the study of hydrogel poly(N-isopropylacrylamide), in which polarization is limited within confined segments of the polymer chain. This cannot explain why the capacitance increases with the stretch ratio.[24] In addition, the actual migration length is far longer than the size of the polymer domain or ionic domain mentioned in this study. The strengthening effect of the dielectric coefficient is attributed to the doped ions in some studies,[25] in which the properties at high frequencies are considered to originate from the Brownian motion of hydrogen bonds.[25] This mode cannot account for the influence of ionic concentrations on conductance or on the inflection points mentioned earlier. It also cannot explain the C–\( \lambda \) and G–\( \lambda \) properties at low frequencies. However, this mode reminds us that the hydrogen bonds are influenced by high-frequency input, so that the output signals contain a significant contribution from the damage to macromolecules.

The types of ions have different effects in the free-ion mode.[24] Some equations have been established to predict the variation in conductance with the frequency of the ionic conductor.[7c] However, these studies focus on conductance and high frequency. The ionic skin we discussed is not a conductor and is not suitable for biological entities. The interrelationship between the deformation and salt concentration has been studied. The deformation strain was found to decrease with increasing ionic concentration.[26] There are no systematic studies on the influence of ionic concentration on ionic migration.
capacitance, and conductance. Moreover, the doping concentration, which also requires further investigation, will influence the size and density of the ionic domains.\cite{27} Furthermore, we expect that ionic mass and covalence will influence the output signals significantly at low frequencies according to our aforementioned modes, which requires an in-depth study.

3. Conclusions

In this work, we systematically studied the variations in capacitance and conductance under mechanical stretching of a salt-doped hydrogel-type ionic skin. The capacitance and conductance response were sensitive to the stretching ratio and input frequency. These increased with the stretch ratio to 145% and 1440%, respectively, depending on the input frequency and ionic concentration. The capacitance-to-stretching variation ratio exceeded $\approx 0.25$, and that of the conductance-to-stretching ratio could reach 0.7. The capacitance decreased with increasing frequency, while the conductance increased. Both the capacitance and conductance relative to the stretch ratio reached an inflection point when the input frequency was fixed. An ionic domain model was established to explain the experimental results. Under external stretching, the ionic domains deform adaptively and release active ions. The external electric field drives some movable ions to the electrode, which greatly enhances the electrical polarization. A portion of the movable ions become free ions in the matrix, which enhances the conductance. The activated ions will be depleted under a critical value of either strain or input frequency. Our study confirms the choice of a salt-doped hydrogel as the matrix of ionic skin. This demonstrates that ionic migration in an organic body can provide a set of low-frequency input and signal-handling methods with high flux and high sensitivity.

4. Experimental Section

Figure 1a shows the structure of the ionic skin.\cite{2b} Acrylamide (AAM), $N,N$-methylenebisacrylamide (MBAA), ammonium persulfate (AP), and $N,N,N',N'$-tetramethylethylenediamine (TEMED) were purchased from Sigma Aldrich Ltd. and used as supplied. NaCl, deionized water, and VHB tape (3 M, 4905) are freely available. AAM and NaCl were dissolved in deionized water at concentrations of 0.5 and 2.74 mol L$^{-1}$, respectively, whereas 0.06 wt% of MBAA and 0.17 wt% of AP relative to the mass of the AAM were added as a cross-linking agent and photo-initiator, respectively. Finally, 0.25 wt% of TEMED relative to AAM was added as a cross-linking accelerator. After the prepared solution was uniformly stirred, it was dropped into the groove of a stainless steel mold, slide was placed on it, and solution was allowed to react for 30 min under an ultraviolet (UV) lamp with a power of 15 W at a wavelength of 254 nm (Figure S4, Supporting Information). Some prepared hydrogel laminates were immersed in NaCl solution before use. After the hydrogel laminates were trimmed to the size of the stretching sample, the water on the surface was blown off using a nitrogen gun. The hydrogel layer and VHB and Cu tapes were overlaid sequentially, as shown in Figure 1a. The molecular structures were examined using infrared and Raman spectroscopy. The capacitance and conductance were examined using an impedance analyzer. During the measurements, the relative humidity was $\approx 30\%$.

The experiments involving human subjects have been performed with the full, informed consent of the volunteers.

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.

Keywords

capacitance, conductance, dielectric coupling, frequency, hydrogels, ionic skins, stretching

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