Ionic Skin

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Our skin is a stretchable, large-area sheet of distributed sensors. These properties of skin have inspired the development of mimics, with differing levels of sophistication, to enable wearable or implantable electronics for entertainment and healthcare. This rapidly growing field of research has recently been thoroughly reviewed. “Electronic skin” is generally taken to be a stretchable sheet with area above 10 cm² carrying sensors for various stimuli, including deformation, pressure, light and temperature. The sensors report signals through stretchable electrical conductors (e.g., carbon grease, microcracked metal films, serpentine metal lines, graphene sheets, carbon nanotubes, silver nanowires, gold nanomeshes, and liquid metals). These conductors transmit signals using electrons. They meet the essential requirements of conductivity and stretchability, but struggle to meet additional requirements in specific applications, such as biocompatibility in biomimetic sensors and transparency in tunable optics.

In contrast, sensors in our skin report signals using ions. Here we explore the potential of ionic conductors in the development of a new type of sensory sheet, which we call “ionic skin”. The sensory sheet is highly stretchable, transparent, and biocompatible. It readily monitors large deformation, such as that generated by the bending of a finger. It detects stimuli with wide dynamic range (strains from 1% to 500%). It measures pressure as low as 1 kPa, with small drift over many cycles. A sheet of distributed sensors covering a large area can report the location and pressure of touch. High transparency allows the sensory sheet to transmit electrical signals without impeding optical signals.

Many ionic conductors, such as hydrogels and ionogels, are highly stretchable and transparent. These gels are polymeric networks swollen with water or ionic liquids. They behave like elastic solids and eliminate the need for containers as required in the case of liquid metal conductors. Whereas familiar elastic gels, such as Jell-O, are brittle and easily rupture, the recent decade has seen the development of hydrogels and ionogels as tough as elastomers. Many hydrogels are bio-compatible. They can be made softer than tissues, achieving the “mechanical invisibility” required for biometric sensors, which monitor soft tissues without constraining them. Although most hydrogels dry out in open air, hydrogels containing humectants retain water in environment of low humidity, and ionogels are non-volatile in vacuum.

We have recently used ionic conductors — together with stretchable and transparent dielectrics — to make actuators, which deform in response to high voltages, on the order of kilovolts. In contrast, the sensors described here deform in response to applied forces, giving signals that can be measured using voltages below 1 V. To illustrate principles in our design of the ionic skin, consider a simple example — a dielectric sandwiched between two ionic conductors (Figure 1). In many applications, the ionic skin reports signals ultimately to external electronic equipment. We form a hybrid ionic-electronic circuit by connecting the ionic skin to electronic conductors, in regions outside the active area of the sensory skin, using thin lines of the ionic conductors. These ionic interconnects mimic the function of axons, and can be as long as meters, if required by an application. Both the dielectric and the ionic conductors are stretchable and transparent, whereas the electronic conductors can be made of stiff and opaque metals. This design allows a large-area sheet of distributed sensors to be highly stretchable and transparent.

To allow repeated use over a long time, we design the hybrid ionic-electronic circuit to transmit electrical signals without electrochemical reaction. Electrical double layers form at the interfaces between the electrodes and the ionic conductors, as well as at the interfaces between the ionic conductors and the dielectric. For many combinations of electrodes and ionic conductors, when no voltage is applied between the two electrodes, the layered structure reaches a state of thermodynamic equilibrium, the “voltage-off” state (Figure 1a). When a voltage is applied between the two electrodes, (so long as the additional voltage across the interface between the electrode and ionic conductor is within a range, e.g., between −1 V and +1 V), electrons and ions do not cross the interface, no electrochemical reaction occurs, and the structure reaches a new state of thermodynamic equilibrium, the “voltage-on” state (Figure 1b). The applied voltage causes additional electric charges and potential through the layered structure (Figure S1, Supporting Information). The electrical double layer at each interface between a metallic electrode and an ionic conductor behaves like a capacitor, in

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series with the capacitor due to the dielectric (Figure 1c). The capacitance $C$ measured between the two electrodes relates to the capacitance of the dielectric $C_D$ and the capacitances of the electrical double layers $C_{EDL}$ as $C = C_D + 1/C_{EDL}$. Charges in the electrode and in the ionic conductor are separated over nanometers, but charges on the two faces of the dielectric are separated by its thickness (on the order of 0.1 mm in our experiments). Consequently, the electrical double layer has a large capacitance compared to the dielectric, $C_{EDL} / C = 10^5$, and the measured capacitance is dominated by that of the dielectric, $C \approx C_D$. Nearly all the voltage applied between the two electrodes drops across the dielectric, and the additional voltage across the electrical double layer is much smaller than 1 V. The fact that the voltage across the electrical double layer is small prevents electrochemical reaction.

When external forces deform the dielectric, the capacitance of this part of the circuit increases (Figure 1d,e). A measurement of this change in capacitance enables the ionic skin to sense the deformation. When a hydrogel serves as a resistive strain sensor, the use of low-voltage AC signals to measure impedance avoids electrochemical reactions. In contrast, our design averts electrochemical reactions by taking advantage of the orders-of-magnitude higher capacitance of the electrical double layers relative to the dielectric. The ionic skin is, thus, a capacitive sensor. It is known that capacitive sensors achieve the highest precision of all electrical sensors, have simple and robust structures, feature high sensitivity and resolution, and allow long-term, drift-free sensing even when temperature changes.

We next derive the relation between deformation and capacitance. We adopt the model of ideal dielectric elastomers, assuming that the volume and permittivity remain constant as the elastomers deform. When a dielectric sheet is stretched by factors $\lambda_1$ and $\lambda_2$ in its plane, the thickness of the sheet scales by factor $\lambda_3 = 1/\lambda_1 \lambda_2$, and the capacitance of the dielectric scales as $C = C_0 (\lambda_1 \lambda_2)^2$, where $C_0$ is the capacitance of the dielectric in the undeformed state. When a uniaxial force stretches a dielectric to $\lambda$ times its initial length, both the width and the thickness of the dielectric reduce by a factor $\sqrt{\lambda}$, and the capacitance of the dielectric scales as $C = C_0 \lambda^2$. When equibiaxial forces stretch a dielectric to $\lambda$ times its initial length in both directions, the capacitance of dielectric elastomer scales as $C = C_0 \lambda^4$.

We demonstrated a strain sensor by using a polyacrylamide hydrogel containing NaCl as the ionic conductor, and an acrylic elastomer (VHB 4905, 3M) as the dielectric (Figure 2). Both materials are highly stretchable and transparent. VHB is marketed as a double-sided adhesive tape. The adhesion between the ionic skin and the finger was adequate and no debonding occurred. VHB exhibits pronounced viscoelastic behavior. The
viscoelastic effects can be minimized by using other dielectric materials (such as polydimethylsiloxane), but we will not pursue this issue in this paper. To limit the evaporation of water from the hydrogels, we covered them with two layers of VHB (Figure 2a). This type of encapsulation was sufficient to reduce the evaporation of water to a negligible level during the duration of the reported experiments.

The softness of the ionic skin allows it to conform readily to dynamic, curved surfaces. We attached the ionic skin on a straight finger (Figure 2b). When the finger bent, the ionic skin stretched and followed to the movement of the joint (Figure 2c). As the finger bent repeatedly, we recorded the capacitance of the ionic skin using a simple capacitance meter (LCR/ESR meter, Model 885, BK Precision), set to a sinusoidal measurement signal of 1 V and 100 Hz (Figure 2d and Video S1 in the Supporting Information). During large deformations, the ionic skin remained adherent to the finger and highly transparent (Figure 2e).

The strain sensor has a large dynamic range and is stable over more than 1000 cycles. We clamped our device at each end between acrylic plates (Figure S2, Supporting Information), stretched it using a mechanical testing apparatus (Instron, Model 3342) with a 50 N load cell at a strain rate of 0.5 min⁻¹, and measured the capacitance using a capacitance meter (Agilent, E4980A) with a voltage of 1 V at a frequency of 20 kHz. The ionic skin could be stretched to about six times the initial length of the strip (Figure 3a,b). The experimentally measured capacitance increased linearly with the stretch, and matched well with the theoretical prediction, $C = C_0 \lambda$ (Figure 3c). At large stretches near rupture, the measured capacitance was slightly lower than that of the theoretical prediction. We did not observe any sliding and fracture, and attributed the deviation of the capacitance to a lowering of the permittivity of the dielectric at large strain. We also stretched the ionic skin by cyclic uniaxial force at a frequency of 1 Hz and a maximum strain of 2%. The change in capacitance of the sensor followed the change in strain, and the drift of capacitance was within 5% over 4000 cycles (Figure 3d, and Figure S3 in the Supporting Information).

We designed and fabricated a stretcher to pull an ionic skin under equi-biaxial conditions (Figure 3e,f, and Figure S4 and Video S2 in the Supporting Information). When the stretcher fixed the ionic skin to a state of biaxial stretch, we took a photo and determined the level of stretch by analyzing the area of the dielectric covered by the conductors. We fabricated strain sensors using VHB and two types of conductors: hydrogel and carbon grease. These strain sensors exhibited nearly identical capacitance-stretch curves (Figure 3g). At high stretches, the measured capacitances of the strain sensors were somewhat lower than the theoretical prediction, $C = C_0 \lambda^4$, which can again...
be attributed to a lowering of the permittivity of the dielectric at high strain.

The ionic skin also readily functions as a pressure sensor. We fabricated a pressure sensor of dimensions 10 mm × 10 mm × 2.4 mm (Figure 4a). The pressure sensor was placed between two grounded metal stages, and a small amount of mineral oil was applied on the surfaces of the sensor to reduce the adhesion and friction between the sensor and the stages (Figure 4b). As the mechanical testing apparatus compressed the sensor at a strain rate of 0.5 min⁻¹, the capacitance of the sensor was measured. The two layers of the hydrogel raised the height of the pressure sensor relative to the surrounding elastomer, so that the testing machine applied the force on the pressure sensor. As the pressure sensor was compressed in thickness, its area expanded. The expansion of the pressure sensor was somewhat constrained by the surrounding elastomer. This constraint stiffened the response of the pressure sensor, but still allowed significant change in capacitance (Figure 4c). The pressure was defined as the applied force divided by the area of the undeformed dielectric elastomer. The pressure sensor was also compressed repeatedly with a prescribed maximum strain of 1% at a frequency 0.5 Hz, while the capacitance and pressure were recorded (Figure 4d). The capacitance–pressure curves were stable over 1000 cycles (Figure 4e, S5). The small reduction in pressure over the cycles was possibly due to viscoelasticity of the materials. For applications that require higher...
sensitivity, one may fabricate the pressure sensor using a compressible dielectric, such as a porous elastomer. This change in design will improve the performance of the sensor when tightly clamped or glued onto a rigid substrate.

We fabricated a sheet of distributed sensors to demonstrate the capability of detecting the location and pressure of touch. The demonstration consisted of four small squares of hydrogel, which lay over a sheet of dielectric, which in turn lay over a single large layer of grounded hydrogel (Figure 5a). A rotational switch connected the four sensors, one at a time, to a capacitance meter (Agilent, E4980A) (Figure 5b), which was controlled by a LabVIEW (National Instruments) program. We attached the sheet on the back of a hand, and pressed the sensors with a finger (Figure 5c). The ionic skin detected the location of touch (Figure 5d, and Video S3 in the Supporting Information). The ionic skin readily resolved the pressure of a gentle touch of a finger (<10 kPa). [31] Whereas an on/off button expresses two states, a sensor in our sensory sheet continuously measures the level of pressure (Figure 5e, and Video S4 in the Supporting Information).

We have used ionic conductors to demonstrate a new type of sensory sheets. They are highly stretchable, transparent, and biocompatible. This unique combination of attributes will open doors to applications in wearable or implantable electronics. In particular, high transparency will allow the sensory sheets to transmit electrical signals without impeding optical signals. This property will enable optical stimulation, as well as continuous inspection of the surfaces covered by the sensory sheets.

Experimental Section

The hydrogels were synthesized using acrylamide (AAm) (Sigma, A8887) as monomers, N,N-methylenebisacrylamide (MBAA) (Sigma, M7279) as crosslinkers, ammonium persulfate (AP) (Sigma, A9164) as radical initiator, and N,N,N’N’-tetramethylethylenediamine (TEMED) (Sigma, T7024) as a crosslinking accelerator.

The gels were prepared by dissolving AAm monomer powder and NaCl into deionized water. Molar concentrations of AAm and NaCl were fixed as 2.2 M and 2.74 M, respectively, throughout the entire experiments. MBAA 0.06 wt% and AP 0.17 wt% with respect to the weight of AAm monomer were added as a cross-linker for AAm and a photo initiator, respectively. After degassing in a vacuum chamber, TEMED 0.25 wt% with respect to the weight of AAm monomer were lastly added as an accelerator. The solutions were poured into a mold with a vacancy (100.0 mm × 100.0 mm × 0.1 mm) and covered with a 3 mm thick transparent glass plate. The gels were cured by the ultraviolet light cross-linker (UVC 500, Hoefer) for 20 min with 8 W power and 254 nm wavelength. The gels were then immersed in aqueous solution of the same concentration of NaCl for more than 24 h. The gels absorbed more water and reached a new state of equilibrium, and the thickness of the gels was estimated to be 0.2 mm.

Figure 4. Ionic skin used as a pressure sensor. a) Design of the pressure sensor. b) The pressure sensor was placed on a stage of a mechanical testing machine. c) The measured capacitance–pressure curve. The inset shows that the pressure sensor had high resolution in the range of 1 kPa, sensitive enough to detect a gentle touch of a finger. d) The pressure and capacitance of a sensor cyclically compressed to a strain of 1%, at a frequency of 0.5 Hz. e) Pressure–capacitance curves were measured for more than 1000 cycles. Four representative cycles are shown.
The gels were cut into the desired shape by using a laser cutting system (VersaLaser VLS3.50, Universal Laser Systems) with 50 W power and 14 cm/s beam speed. Before stacking hydrogel on top of VHB, the surfaces of the hydrogels were dried with N₂ gas for 1 min to improve the adhesion between gel and VHB by removing water from the gel surfaces. A dielectric layer was sandwiched between two layers of the hydrogel, resulting in a capacitive sensor. An extra two layers of VHB were attached to the top and bottom of the sensor to insulate the sensor and prevent evaporation of the hydrogel.

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

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