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Ionotactile Stimulation: Nonvolatile Ionic Gels for Human−Machine Interfaces

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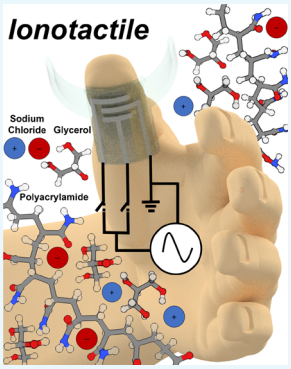
Supporting Information

ABSTRACT: We report the application of a nonvolatile ionic gel as a soft, conductive interface for electrotactile stimulation. Materials characterization reveals that, compared to a conventional ionic hydrogel, a glycerol-containing ionic gel does not dry out in air, has better adhesion to skin, and exhibits a similar impedance spectrum in the range of physiological frequencies. Moreover, psychophysical experiments reveal that the nonvolatile gel also exhibits a wider window of comfortable electrotactile stimulation. Finally, a simple pixelated device is fabricated to demonstrate spatial resolution of the haptic signal.



INTRODUCTION

The skin is the body's largest organ.[1] It is equipped with a variety of sensing functionalities with which electronic devices can be interfaced to transmit information to the brain. The tactile sense thus provides a natural route for augmenting human−machine interactions. Electrotactile stimulation is one way for information to be communicated through the skin—in the form of a locally resolved tingling sensation.[2] Conventional electrotactile devices use metallic conductors to couple capacitively with ions in cutaneous tissue, activate nerve afferents, and manifest as a sensation of touch. In this report, we introduce a new concept: the use of a nonvolatile, ionically conductive gel as a soft interface between the rigid electronic circuitry of machines and the natural ionic circuitry of humans (Figure 1).

The rapidly advancing field of stretchable electronics is changing the way devices are designed—especially those meant to interface with humans.[3,4] Architectures for electrotactile devices have evolved accordingly. Originally designed using conventional electronic materials, electrotactile devices were restricted to rigid surfaces.[2] Such devices were explored for programmable braille and displays for the visually impaired.[5] More recently, advances in fabrication methods have enabled the development of conformable devices that use geometrically patterned electronic conductors on the surface of elastomers to improve the interface for electrotactile stimulation.[6,7] Such devices make use of materials that are intrinsically rigid and thus require to be patterned into thin serpentine structures that can withstand strain and conform to the skin.

Ionic hydrogels have concurrently emerged as promising conductors for a variety of sensing and actuation applications because of their optical transparency, mechanical softness, biocompatibility, and capacity to self-heal.[8−10] This unique combination of properties has enabled the development of

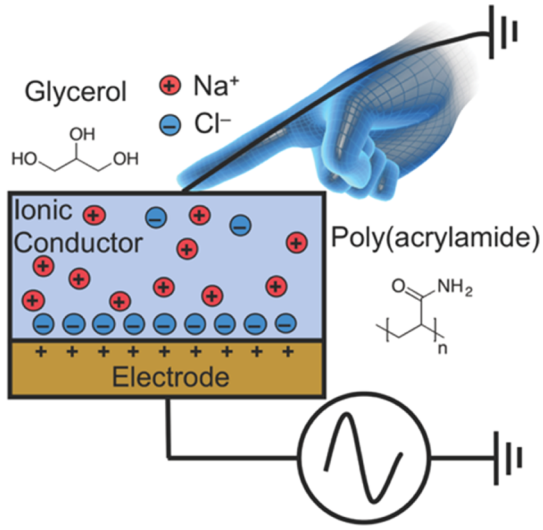


Figure 1. Schematic diagram illustrating the concept of an ionotactile device in a monopolar stimulation configuration. A soft and deformable ionic conductor is used to interface a metallic electrode and human skin.

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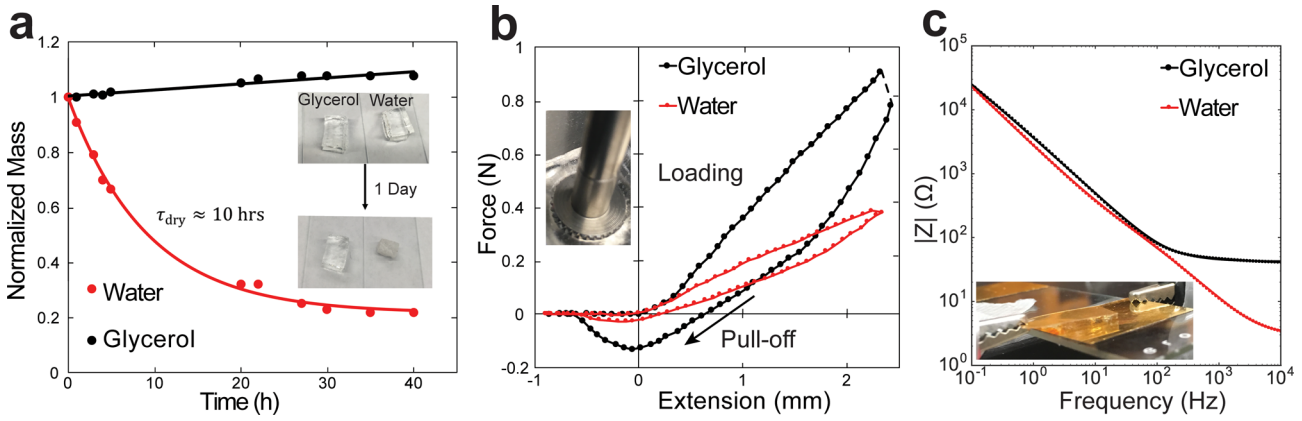

Figure 2. Materials characterization. (a) Normalized mass as a function of time under ambient conditions demonstrating the stability of the ionic glycerol gel in air. Insets show photographs of gels before and after experiments. (b) Indentation and pull-off curves obtained using the cylindrical stainless steel punch shown in the inset. (c) Electrochemical impedance spectra obtained using the parallel-plate capacitor geometry shown in the inset.

several novel applications such as transparent loudspeakers,[11] wearable sensors,[12−14] underwater microphones,[15] and electroluminescent devices.[16,17] These materials can also be three-dimensionally (3D) printed[18,19] and chemically bonded to diverse surfaces[20,21] enabling cheap, rapid, and precise manufacturing of robust devices. Such creative demonstrations have inspired us to consider this class of materials as potentially useful for providing electrotactile stimulation as part of a soft haptic device.

RESULTS AND DISCUSSION

As a first demonstration, we used a standard poly(acrylamide) (PAAm) hydrogel containing an aqueous sodium chloride (NaCl, 2.74 M) solution. PAAm has a modulus commensurate with that of biological tissue (~10 kPa), it is biocompatible, and its polymerization chemistry is compatible with 3D-printing technology.[18,19] A function generator was used to pass a square wave alternating current through the hydrogel into the index finger of a subject. Upon contacting the hydrogel with an electrically grounded finger in a monopolar configuration,[22] a mild tingling sensation was perceived. As the force applied by the finger was increased, the sensation grew stronger.

Evaporation of water from the ionic hydrogel is a particularly important obstacle in this application because the device geometry requires the hydrogel to be exposed to air, and thus encapsulation is not an option. Ionic liquids[23] and highly hydratable salts such as lithium chloride[24] have been proposed as strategies to mitigate drying; however, these liquids are acutely toxic and thus cannot be used in place of salt water for a device designed to come in contact with skin. To overcome this constraint, we replaced the salt water with a solution of glycerol containing 0.7 M NaCl. Glycerol is a biocompatible, low vapor pressure fluid (T_B = 290 °C) that is capable of dissolving ions, albeit at lower concentrations than can water. Replacement of the water was achieved by simply soaking a hydrated hydrogel in the glycerol solution overnight. This process led to an observable shrinkage of the gel; a ~60% reduction in volume was measured using calipers. Mass loss experiments, shown in Figure 2a, revealed that the replacement of water with the glycerol solution resulted in a conductive gel that was stable in air. The water rapidly evaporated from the aqueous hydrogel under ambient conditions with a mass decay time of approximately 10 h, while the glycerol gel absorbed some moisture from the air to increase its mass slightly before reaching equilibrium. Due to the hydroscopic nature of glycerol, it can be expected that fluctuations in the relative humidity of the environment will lead to minor changes in the equilibrium concentration of water in the glycerol gel.

In handling the two materials, we observed that the glycerol gel adhered to the finger more strongly than the hydrogel did. Such adhesive properties are desirable for maintaining a stable interface with the user's skin during use of a device. To compare the adhesive and mechanical properties of these two materials, we performed mechanical indentation experiments on rectangular slabs using a stainless steel cylindrical punch. As shown in Figure 2b, we found that the glycerol gel exhibited both a stiffer response to indentation, as well as a significantly stronger pull-off force. The elastic modulus was extracted from these curves using an appropriate model[25] to correct for the finite thickness of the hydrogel sample (see Supporting Information, section 1). We found that the aqueous ionic hydrogel had a compressive elastic modulus of 27 kPa, whereas the glycerol gel had a higher value of 80 kPa. This increase in stiffness was consistent with the observed shrinkage of the gel upon replacing water with glycerol. Moreover, the pull-off force for the glycerol gel was an order of magnitude larger than that of the hydrogel, in agreement with our qualitative observation of improved adhesion with the skin.

It was expected that the replacement of water with glycerol would increase the electrical impedance due to a lower concentration of ions and higher viscosity. Electrochemical impedance spectroscopy was used to characterize the electrical response of the two materials. Gold electrodes, sputtered onto flexible poly(ethylene terephthalate) (PET) films, were used as electrodes in a parallel-plate capacitor geometry (1 cm × 1 cm × 0.2 cm). Figure 2c shows the measured impedance spectrum. The glycerol gel exhibited a slightly higher impedance over the frequency range relevant for electrotactile stimulation (1−1000 Hz); however, order-of-magnitude differences only occured at frequencies over 1000 Hz, suggesting that these two materials should behave comparably in ionotactile devices. A more detailed analysis of the impedance data using equivalent circuit modeling is provided in section 2 of the Supporting Information; this analysis revealed that the series resistance of the glycerol gel was approximately an order of magnitude greater than that of the hydrogel.

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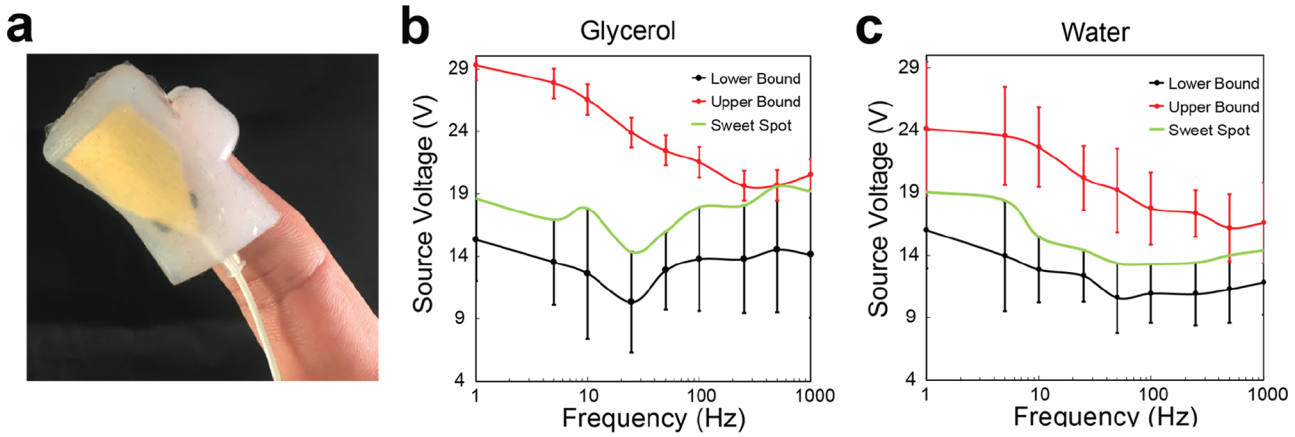

Figure 3. Ionotactile device characterization. (a) Image of device worn on the index finger. Sensation curves showing the source voltage required for stimulation for a range of frequencies for (b) glycerol and (c) water. Error bars show the standard deviation between four subjects.

To determine sensation threshold curves, a simple finger stimulator device was fabricated using a mold-casting process described in the Supporting Information, section 4. Ecoflex 00-30 was used as the housing material (Figure 3a), and the ionic gel was addressed using a film of PET containing a film of sputtered gold. We note here that over the course of our electrical stimulation experiments, we did not observe any changes in the appearance or electrical properties of the device, indicating that no irreversible electrochemical reactions occurred at the electrode interface. Magnets embedded within the Ecoflex were used to attach the device to the user's finger. We tested the device performance using simple psychophysical experiments on a pool of four subjects. Experiments were performed using the "method of adjustment", where subjects manually adjusted the voltage until they perceived a sensation, corresponding to the lower bound for tactile stimulation. Once a lower bound was determined, subjects increased the voltage until they felt like the sensation would no longer be considered comfortable to determine an upper bound. A wide range of frequencies were tested to construct the sensation curves shown in Figure 3b,c.

In agreement with our impedance measurements, we found that the glycerol gel exhibited comparable performance to the hydrogel when incorporated into the device. For both materials, subjects observed that below 10 Hz, individual pulsations were discernible, whereas above 10 Hz, only a continuous tingling sensation was perceived. Such experiments are inherently subjective; therefore, the observed variance across subjects was not surprising. Interestingly, we found that in the range of 1–100 Hz, the glycerol gel had a larger window of comfortable stimulation. For both materials, we constructed a voltage–frequency curve that corresponds to a "sweet spot" for comfortable stimulation that would be perceptible to all users. This was obtained by simply adding the standard deviation to the average of the lower bound for stimulation.

To demonstrate spatial discrimination, a pixelated device was fabricated (Figure 4). The electrodes were designed such that the middle pixel was a common ground, whereas the upper and lower pixels applied the stimulating voltage, corresponding to a bipolar electrode configuration.[26] Films of Mylar (aluminum-coated PET films) were used to electrically address the pixels. With this design, we found that the two stimulating pixels could be distinguished by the user; this experiment demonstrated that spatial resolution was possible. We also found that the

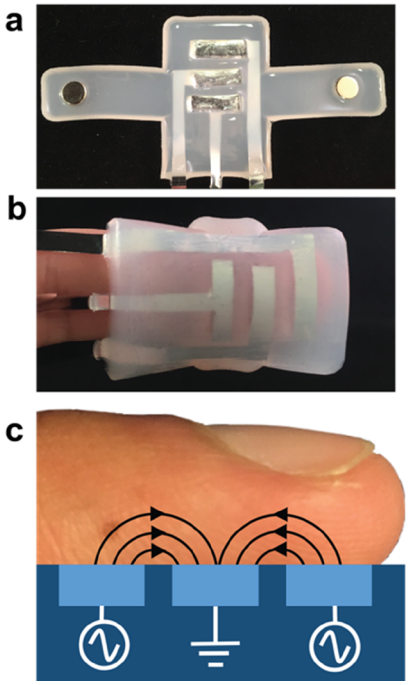

Figure 4. Pixelated ionotactile device. (a) Top-down view of device. The middle electrode is the common ground, whereas the top and bottom electrodes are stimulating pixels. (b) Device worn on a finger. (c) Schematic diagram showing the electric field lines associated with a bipolar stimulation geometry.

threshold voltage for sensation was significantly higher: approximately 80 V at 50 Hz. We expect that the use of 3D-printing technology to pattern the electrodes into a concentric design comprising an inner disk and an outer ring[6] would facilitate more localized tactile sensations at a lower stimulating voltage. Finally, it is important to note that humans naturally integrate visual and haptic signals.[27] Therefore, a wider range of tactile sensations could be accessible when such a device is paired with visual stimuli.

CONCLUSIONS

We have developed a nonvolatile, transparent, ion-conducting gel to demonstrate a materials innovation in haptic technology: an ionotactile device. This device enables an improved route for human–machine interaction and has potential to be integrated

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with emerging technologies such as virtual and augmented reality. We found that the use of a saline glycerol PAAm gel was superior to a conventional ionic hydrogel because of its stability in air, improved adhesion with the user, and a larger window for comfortable electrical stimulation in the range of 1−100 Hz. One potential extension of this technology would be to create a multimodal device that is capable of simultaneously sensing mechanical deformations[12] and responding by sending a haptic signal to the user. This multimodal functionality, in conjunction with tissue-like mechanical properties, makes the ionic gel a particularly attractive material for robot-assisted telesurgery applications.[28]

EXPERIMENTAL METHODS

Synthesis. The ionic hydrogels were synthesized following a procedure described previously.[1] Sodium chloride, acrylamide (AAm), *N*,*N*-methylenebisacrylamide (MBAA), ammonium persulfate (AP), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were all purchased from Sigma-Aldrich and used as received. A solution of NaCl (2.74 M), AAm (2.2 M), MBAA (0.06 wt %), and AP (0.17 wt %) (with respect to the weight of AAm) in deionized water was prepared. The solution was subsequently degassed in a Schlenk flask by three evacuate/refill cycles. TEMED (0.25 wt % with respect to AAm monomer) was injected into the flask, and the solution was quickly poured into a mold for curing. The mold was fabricated using a glass Petri dish and a pour-casted/plasma-treated (5 mm thick) poly(dimethysiloxane) slab:Sylgard-184, 20:1 base to curing agent with a 4 × 4″ square cutout. The prepolymer solution was covered with a glass slide and then exposed to ultraviolet light using a nail polish curing station for 20 min. The gels were then immersed in an aqueous 2.74 M NaCl solution for 24 h and finally rinsed three times with fresh saline solution to remove unreacted monomer and catalyst. Replacement of water with glycerol was achieved by rinsing the ionic hydrogel with deionized water and then immersing it in a 0.7 M NaCl in glycerol solution for 24 h. Before use, all gels were patted dry with paper towels and cut into the desired geometries using a razor blade.

Electrochemical Impedance Spectroscopy. Impedance measurements were conducted over the range of 1−10 000 Hz using a Solartron 1260 impedance analyzer with a dc bias of 0 V and an applied ac voltage of 10 mV. Gold films sputtered onto PET (60 nm) were used as the blocking electrodes in a parallel plate capacitor geometry (1 cm × 1 cm × 0.2 cm). Equivalent circuit modeling was performed with ZView software.

Sensation Experiments. Electrotactile sensation experiments were performed using a Siglent SDG 2042X function generator. A total of four subjects were tested. These subjects were authors on this work, and informed consent was obtained. The subject's hand was electrically grounded using 3M Red Dot Foam electrodes. Subjects were instructed to start at 2 V and gradually increase the voltage in increments of 0.2 V until they perceived a sensation. Once the sensation threshold had been determined, subjects were instructed to continue increasing the voltage at the same rate until they felt the sensation would become uncomfortable if increased any further. Subjects were asked to describe the sensation for each frequency tested.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01773.

Mechanical indentation analysis, equivalent circuit modeling, Fourier transform infrared spectroscopy, and device fabrication (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) McGrath, J. A.; Uitto, J. Anatomy and Organization of Human Skin. *Rook's Textbook of Dermatology*, 8th ed.; Blackwell Publishing: New Jersey, 2010.

(2) Kajimoto, H.; Kawakami, N.; Maeda, T.; Tachi, S. Electro-Tactile Display with Tactile Primary Color Approach. *Proceedings of International Conference on Intelligent Robots and Systems*, 2004; Vol. *10*, pp 1−13.

(3) Wang, H.; Ma, X.; Hao, Y. Electronic Devices for Human-Machine Interfaces. *Adv. Mater. Interfaces* **2017**, *4*, 1600709.

(4) Kim, J.; Lee, M.; Shim, H. J.; Ghaffari, R.; Cho, H. R.; Son, D.; Jung, Y. H.; Soh, M.; Choi, C.; Jung, S.; et al. Stretchable Silicon Nanoribbon Electronics for Skin Prosthesis. *Nat. Commun.* **2014**, *5*, 5747.

(5) Bach-y-rita, P.; Tyler, M. E.; Kaczmarek, K. A. Seeing with the Brain. *Int. J. Hum. Comput. Interact.* **2003**, *15*, 285−295.

(6) Ying, M.; Bonifas, A. P.; Lu, N.; Su, Y.; Li, R.; Cheng, H.; Ameen, A.; Huang, Y.; Rogers, J. A. Silicon Nanomembranes for Fingertip Electronics. *Nanotechnology* **2012**, *23*, 344004.

(7) Lim, S.; Son, D.; Kim, J.; Lee, Y. B.; Song, J.-K.; Choi, S.; Lee, D. J.; Kim, J. H.; Lee, M.; Hyeon, T.; et al. Transparent and Stretchable Interactive Human Machine Interface Based on Patterned Graphene Heterostructures. *Adv. Funct. Mater.* **2015**, *25*, 375−383.

(8) Keplinger, C.; Sun, J.-Y.; Foo, C. C.; Rothemund, P.; Whitesides, G. M.; Suo, Z. Stretchable, Transparent, Ionic Conductors. *Science* **2013**, *341*, 984−987.

(9) Rogers, J. A. A Clear Advance in Soft Actuators. *Science* **2013**, *341*, 968−969.

(10) Cao, Y.; Morrissey, T. G.; Acome, E.; Allec, S. I.; Wong, B. M.; Keplinger, C.; Wang, C. A Transparent, Self-Healing, Highly Stretchable Ionic Conductor. *Adv. Mater.* **2017**, *29*, 1605099.

DOI: 10.1021/acsomega.7b01773
ACS Omega 2018, 3, 662−666

(11) Keplinger, C.; Sun, J.-Y.; Foo, C. C.; Rothemund, P.; Whitesides, G. M.; Suo, Z. Stretchable, Transparent, Ionic Conductors. *Science* **2013**, *341*, 984−987.
(12) Sun, J.-Y.; Keplinger, C.; Whitesides, G. M.; Suo, Z. Ionic Skin. *Adv. Mater.* **2014**, *26*, 7608−7614.
(13) Kim, C.-C.; Lee, H.-H.; Oh, K. H.; Sun, J.-Y. Highly Stretchable, Transparent Ionic Touch Panel. *Science* **2016**, *353*, 682−687.
(14) Sarwar, M. S.; Dobashi, Y.; Preston, C.; Wyss, J. K. M.; Mirabbasi, S.; David, J.; Madden, W. Bend, Stretch, and Touch: Locating a Finger on an Actively Deformed Transparent Sensor Array. *Sci. Adv.* **2017**, *3*, No. e1602200.
(15) Gao, Y.; Song, J.; Li, S.; Elowsky, C.; Zhou, Y.; Ducharme, S.; Chen, Y. M.; Zhou, Q.; Tan, L. Hydrogel Microphones for Stealthy Underwater Listening. *Nat. Commun.* **2016**, *7*, 12316.
(16) Yang, C. H.; Chen, B.; Zhou, J.; Chen, Y. M.; Suo, Z. Electroluminescence of Giant Stretchability. *Adv. Mater.* **2016**, *28*, 4480−4484.
(17) Larson, C.; Peele, B.; Li, S.; Robinson, S.; Totaro, M.; Beccai, L.; Mazzolai, B.; Shepherd, R. Highly Stretchable Electroluminescent Skin for Optical Signaling and Tactile Sensing. *Science* **2016**, *351*, 1071−1074.
(18) Barry, R. A.; Shepherd, R. F.; Hanson, J. N.; Nuzzo, R. G.; Wiltzius, P.; Lewis, J. A. Direct-Write Assembly of 3D Hydrogel Scaffolds for Guided Cell Growth. *Adv. Mater.* **2009**, *21*, 2407−2410.
(19) Tian, K.; Bae, J.; Bakarich, S. E.; Yang, C.; Gately, R. D.; Spinks, G. M.; in het Panhuis, M.; Suo, Z.; Vlassak, J. J. 3D Printing of Transparent and Conductive Heterogeneous Hydrogel-Elastomer Systems. *Adv. Mater.* **2017**, *29*, 1604827.
(20) Yuk, H.; Zhang, T.; Lin, S.; Parada, G. A.; Zhao, X. Tough Bonding of Hydrogels to Diverse Non-Porous Surfaces. *Nat. Mater.* **2015**, *15*, 190−196.
(21) Yuk, H.; Zhang, T.; Parada, G. A.; Liu, X.; Zhao, X. Skin-Inspired Hydrogel−elastomer Hybrids with Robust Interfaces and Functional Microstructures. *Nat. Commun.* **2016**, *7*, 12028.
(22) Merrill, D. R.; Bikson, M.; Jefferys, J. G. R. Electrical Stimulation of Excitable Tissue: Design of Efficacious and Safe Protocols. *J. Neurosci. Methods* **2005**, *141*, 171−198.
(23) Chen, B.; Lu, J. J.; Yang, C. H.; Yang, J. H.; Zhou, J.; Chen, Y. M.; Suo, Z. Highly Stretchable and Transparent Ionogels as Nonvolatile Conductors for Dielectric Elastomer Transducers. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7840−7845.
(24) Bai, Y.; Chen, B.; Xiang, F.; Zhou, J.; Wang, H.; Suo, Z. Transparent Hydrogel with Enhanced Water Retention Capacity by Introducing Highly Hydratable Salt. *Appl. Phys. Lett.* **2014**, *105*, 151903.
(25) Shull, K. R.; Ahn, D.; Chen, W.-L.; Flanigan, C. M.; Crosby, A. J. Axisymmetric Adhesion Tests of Soft Materials. *Macromol. Chem. Phys.* **1998**, *199*, 489−511.
(26) Comte, P. Monopolar versus Bipolar Stimulation. *Proceedings of 8th Meeting World Society Stereotactic and Functional Neurosurgery*, 1981; Vol. 45, Part I, pp 156−159.
(27) Ernst, M. O.; Banks, M. S. Humans Integrate Visual and Haptic Information in a Statistically Optimal Fashion. *Nature* **2002**, *415*, 429−433.
(28) Marescaux, J.; Leroy, J.; Gagner, M.; Rubino, F.; Mutter, D.; Vix, M.; Butner, S. E.; Smith, M. K. Transatlantic Robot-Assisted Telesurgery. *Nature* **2001**, *413*, 379−380.

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ACS Omega 2018, 3, 662−666