

Supporting Information

to

Ion Sensing with Thread-based Potentiometric Electrodes

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Materials

Potassium ionophore I (valinomycin), sodium ionophores X (4-tert-Butylcalix[4]arene-tetraacetic acid tetraethyl ester), calcium ionophore II (N,N,N',N'-Tetra[cyclohexyl]diglycolic acid diamide, N,N,N',N'-Tetracyclohexyl-3-oxapentanediamide), potassium tetrakis(4-chlorophenyl)borate (KTPCIB, Selectophore grade), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB, Selectophore grade), 2-nitrophenyl octyl ether (*o*-NPOE, Selectophore grade), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF, inhibitor-free, for HPLC, purity $\geq 99.9\%$), sodium dodecylbenzenesulfonate (SDBS), multi-walled carbon nanotubes (6–9 nm x 5 μm), and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, 5 wt %, screen-printable ink) were purchased from Sigma-Aldrich. Carbon graphite ink was purchased from Ercon (Wareham, MA). Carbon black (BP 2000, LOT-3917778) was provided by CABOT (Alpharetta, Georgia). Polyolefin heat-shrinkable tubing (product of Uxcel), Carbon Fiber Tow (UTS50 Tenax-E, product of Toho Tenax), cotton thread (100% mercerized crochet thread, Aunt Lydia's Classic 10, product of Coats), 3-ply Nylon (Nylon Twine, product of Katzco), and polypropylene (Twisted Mason Line, product of Home Depot) were purchased from Amazon. Polystyrene tipped swabs for applying inks to thread were purchased from Puritan Medical Products. The Hach Chloride QuanTab test strips (low range and high range) were purchased from Amazon. The sand (Quikrete All-purpose sand (50 lb) and soil (Premium Topsoil, Scotts (0.75 cu. ft.)) were bought at Home Depot, Watertown, MA. Blood serum (from human male AB plasma, USA origin, sterile-filtered) and urine (human, pooled) were purchased from Sigma-Aldrich. Coconut water (product of VITA COCO) and calcium supplement (product of Nature Made) were purchased from CVS pharmacy.

Polyolefin heat-shrinkable tubing (product of Uxcel), and nail polish (Instadri, Sally Hansen) were purchased from Amazon.

Preparation of Inks

We prepared two inks: (i) ink made with an organic solvent, polymer, plasticizer, and carbon black, and (ii) an aqueous ink made with carbon nanotubes and surfactant. We prepared the carbon black ink by grinding (five minutes, with a mortar and pestle) 0.2 g of carbon black powder, 0.533 g of *o*-NPOE, 0.267 g of PVC, 1 mL of THF, and 4 mL of cyclohexanone. We applied this ink to the thread immediately after preparation. We prepared the aqueous carbon nanotube ink (according to a previously described procedure¹) by making a mixture of 3 mg/mL MWCNTs and 10 mg/mL SDBS in deionized water, placing the mixture in an ice bath, and sonicating the mixture (using a tip sonicator, Branson sonifier 340 with an output power of 400 W) for two hours to create a suspension.

Fabrication of thread-based ISEs

We unwound the 3-ply Nylon and polypropylene yarn into three thinner fiber bundles (≈ 1 mm thickness) and cut these fiber bundles into 8-cm pieces. Cotton thread was used without alteration, and simply cut into 8-cm pieces. We used a polystyrene-tipped swab to apply the conductive inks (graphite, PEDOT:PSS, and carbon black) to the thread and allowed the ink to dry overnight at ambient temperature to generate electrically conductive thread.

To make cotton thread impregnated with carbon nanotubes, we followed a previously described procedure.¹ We dipped the cotton thread in the aqueous carbon nanotube ink (thread acquires a black color immediately), squeezed the thread with a tweezer to remove the excess aqueous solution, gently rinsed the thread with 3–5 mL of deionized water to remove the excess

surfactant (carbon nanotubes also came off during this step, evident from the back color of water coming off the thread), and let the thread dry at ambient temperature for 24 hours. We repeated this process five times.

To fabricate the thread-based ISEs, we attached one end of the conductive thread (coated with graphite, PEDOT:PSS, carbon nanotube, or carbon black inks) to a paper clip, dipped 3 cm of the other end of the thread into the ion-selective solution, and hung the thread vertically to allow the membrane to set overnight at room temperature (the solvent—THF— evaporates and yields a self-supported plastic membrane). We sealed the ISM-coated conductive thread using either of two approaches (Figure 1): (i) We inserted the ISM-coated conductive thread into a 7-cm heat-shrinkable tube, leaving 0.5 cm of thread exposed at each end, and used a heat gun to heat the heat-shrinkable tube for 5–10 s to form a tight fit around the thread, and (ii) Using the brush provided with the nail polish, we painted 7 cm of thread, leaving only 0.5 cm of the ink-coated and ISM-ink-coated thread at each end.

Electrochemical Measurements

For measurement of the electrical potential, we used an EMF 16 channel potentiometer (Lawson Labs, Malvern, PA) controlled with EMF Suite 1.02 software (Lawson Labs). We performed the measurements at room temperature (≈ 25 °C) using a free-flow double-junction Ag/AgCl reference electrode (with a movable ground glass sleeve junction, 1.0 M lithium acetate bridge electrolyte) purchased from Mettler Toledo.

Resistance Measurements

We measured resistivity of ink-coated thread (with inks made of carbon graphite, carbon black, carbon nanotube, and PEDOT:PSS) over 1.0 cm length of the thread, using a digital

multimeter (Fluke Inc. 77IV, Everett, WA, USA). We measured the resistance of the ion-selective membrane (ISM) using the known shunt method.² In brief, we measured the *emf* of ISE in 100 mM KCl for 20 s (V_1), connected the resistor R_{test} (75 k Ω) test between the ISE and the reference electrode, and measured the *emf* of ISE again (V_{test}). We calculated the resistance of the ISE from Equation 1.

Equation 1:
$$R_{ISE} = R_{test} \left(\frac{V_1 - V_{test}}{V_{test}} \right)$$

Since the resistance of the ISM is significantly higher than the conductive inks, we approximated the resistance of the ISE to that of the ISM ($R_{ISE} \approx R_{ISM}$).

Solution Preparation and Calibrations

We prepared all the solutions with deionized purified water (18.2 M Ω .cm specific resistance, EMD Millipore, Philadelphia, PA). We obtained the calibrations by immersing the sensors (five replicates) in different standard solutions, and measuring the *emf*.

Scanning Electron Microscopy

We conducted the scanning electron microscope (SEM) measurements with field emission SEM (Zeiss Ultra 55) at Center for Nanoscale Systems (CNS) of Harvard University. The base pressure was 1.0×10^{-4} mbar and the electron beam energy was at 5.0 keV. We sputter-coated 5.0 nm platinum on non-conductive bare cotton thread prior to SEM imaging.

Effect of the Type of the Ink and the Material of Thread on the Performance of the Sensors

We studied the effect of the ion-to-electron transducer ink and the material of the thread (Nylon, polypropylene, and cotton) to optimize the stability and electrode-to-electrode reproducibility in the potential of the thread-based ISEs.

We initially used a commercial carbon graphite ink (with proprietary hydrophobic polymer binder and solvent) and Nylon thread to fabricate K^+ ISEs (Figure S1 shows an SEM image of this sensor). Numerous studies had shown that graphite can be used as ion-to-electron transducer to provide solid-contact ISEs with stable electrical potentials.³⁻⁵ Figure S2 shows the Nernstian response of this ISE to K^+ (slope: 60.4 ± 4.0 mV/decade). We evaluated the potential stability of the sensors using a protocol that would represent how they will be used in the field; we selected a set of sensors that were not exposed to or soaked in deionized water or a KCl solution (that is, we had not conditioned the sensors), we placed the sensors in 100 mM KCl, and recorded their *emf* for 30 minutes. We report the potential drift of the electrodes over the first five minutes (unless noted otherwise) of their exposure to KCl. The sensors made with Nylon and graphite ink did not exhibit good short-term potential stability (they drifted 0.55 mV/min in the *emf*). Use of a commercially available aqueous ion-to-electron transducer ink based on poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), PEDOT:PSS, and Nylon for fabrication of K^+ ISEs also resulted in Nernstian behavior (Figure S2, slope: 54.0 ± 1.4 mV/decade, E° : 521.3 ± 8.9 mV), but poor potential stability (0.52 mV/min drift in the *emf*). This poor potential stability is probably due to two factors: (i) the presence of surfactants and proprietary additives in the commercial inks that can interfere with the response of the ISEs to ions,^{6,7} and (ii) the low specific capacitance of the thread coated with the inks. The high specific capacitance of the ion-to-electron transducer layer minimizes the drift in the potential of solid-contact ISEs.⁸⁻¹⁰

Figure S3 shows the response of K^+ -selective ISEs made with Nylon, cotton, and polypropylene thread and carbon graphite ink. All K^+ ISEs exhibited μ -molar limits of detection and Nernstian slopes: Nylon (slope: 60.4 ± 4.0 mV/decade, E° : 659.5 ± 26.8 mV), cotton (slope: 55.2 ± 1.4 mV/decade, E° : 488.1 ± 11.2 mV), and polypropylene (slope: 54.1 ± 0.9 mV/decade, E° : 552.1 ± 29.6 mV). We used cotton thread for fabrication of sensors presented beyond this point for three reasons: (i) cotton was available in small diameters (~ 1 mm) and did not require unwinding of the fiber bundle to achieve thinner fiber bundles, (ii) cotton had stronger mechanical strength than the unwound Nylon or polypropylene thread, (iii) cotton absorbed the inks more homogeneously than the Nylon and polypropylene thread, and resulted in sensors with better electrode-to-electrode reproducibility in the slope and E° than did the Nylon and polypropylene thread.

Figure S4 compares the potential stability of K^+ ISEs (made with the carbon black ink and cotton thread) to two previously reported thread-based potentiometric sensors developed for analysis of sweat in wearable devices.^{1,11} Parrilla et al. have demonstrated fabrication of the Na^+ ISE using carbon fiber thread as ion-to-electron transducer and reported excellent potential stability of the sensor (-1.3 mV/h, measured for two hours).¹¹ Carbon fiber thread is made by embedding carbon filaments in a polymer matrix and is mainly used to reinforce composite materials.¹² The advantage of carbon fiber thread is that it is already conductive ($20 \pm 5 \Omega/cm$) and does not need to be coated with an additional ink to become conductive. Therefore, the ISM can be deposited directly on the carbon fiber. Figure S5 confirms that a Nernstian response can be obtained using carbon fiber thread; but poor potential stability (0.7 mV/min drift over five minutes and 1.3 mV/min drift over 30 minutes) prohibits the use of this sensor in point-of-care applications. The differences between the potential stability of carbon-fiber-based sensors

observed by us and by Andrade et al. could originate from two factors: (i) the carbon fiber thread used could be manufactured by different suppliers¹¹, (ii) the protocol used for measuring potential stability could be different (i.e., the sensors could have been conditioned by Andrade et al. prior to the measurement of the potential drift).

We also investigated the use of an aqueous carbon nanotube ink for fabrication of thread-based sensors. We prepared this ink according to a previously established protocol (suspending carbon nanotubes in the aqueous solution using sodium dodecylbenzenesulfonate as surfactant).¹ Andrade et al. have demonstrated that when cotton thread is immersed in this ink, it immediately acquires a black color, demonstrating that carbon nanotubes get embedded in the filaments of cotton. They rinsed the cotton with deionized water to remove the excess surfactants, dried the thread at ambient temperature, and fabricated cotton-based potentiometric sensors with excellent potential stability (less than 250 $\mu\text{V}/\text{h}$ drift).¹

Repeating this protocol, we obtained cotton thread with impregnated with carbon nanotubes with resistance of $14.6 \pm 1.3 \text{ K}\Omega/\text{cm}$. The K^+ ISEs made with this cotton had Nernstian response (Figure S6, slope: $54.5 \pm 1.6 \text{ mV}/\text{decade}$, E° : $523.4 \pm 10.3 \text{ mV}$). Figure S3 shows that the initial drift in the *emf* of these sensors was large (1.1 mV/min drift), but after five minutes, good potential stability was accomplished (0.04 mV/min drift). We maintained use of the carbon black ink for fabrication of thread-based sensors, because of good electrode-to-electrode E° reproducibility and potential stability of sensors made with this ink.

Measurements of Cl^- in Soil

We washed 20 g of each soil sample with 250 mL of deionized water, placed it in an oven (130°C) for one hours to dry, and let the soil reach to room temperature. We measured 2.0 g of

soil and added 5 mL of aqueous chloride containing solution (100 mM, 10 mM, and 1 mM KCl) to the soil, and kept the mixture in a closed container overnight before the measurement. For measurements with the thread-based sensor, we placed the thread-based Cl^- sensor and the reference electrode in the aqueous solution that was in contact with the soil (without any filtration), and recorded the *emf* of the cell after two minutes. We repeated this process for the unwashed soil.

Measurements of Ca^{2+} in the Calcium Dietary Supplement

We recorded the weight of three calcium pills, crushed them into a fine powder, and dissolved 10 mg of this powder in 30 mL of sodium phosphate buffer (pH: 7.5). We calibrated the Ca^{2+} thread-based ISEs in the same phosphate buffer in a range of 10.0–0.1 mM Ca^{2+} , immersed the ISEs in the solution of dietary calcium supplement, and recorded the *emf* values of the ISEs. We calculated the concentration of Ca^{2+} from the *emf* values (as explained in the manuscript) and then back calculated the amount of calcium in one pill.

Measurements in Blood Serum and Urine

Preparation of standards: The standards used for calibrating the ISEs prior to measurement in diluted (20 times) serum or urine contained the following:

Serum standard 1:	0.10 mM KCl and 1.00 mM NaCl
Serum standard 2:	0.25 mM KCl and 5.00 mM NaCl
Serum standard 3:	0.50 mM KCl and 10.00 mM NaCl
Urine standard 1:	1.00 mM KCl and 1.00 mM NaCl
Urine standard 2:	2.50 mM KCl and 5.00 mM NaCl
Urine standard 3:	5.00 mM KCl and 10.00 mM NaCl

Fabrication of the Conventional Ion-Selective Electrodes: We fabricated the ISMs according to protocols established in the literature.^{13,14} The K⁺ sensing membrane consisted of 65.85 wt.% DOS (Bis(2-ethylhexyl) sebacate, Selectophore grade), 32.95 wt.% PVC (Poly(vinyl chloride), Selectophore grade, high molecular weight), 1.00 wt.% Potassium Ionophore I (1.00 %), and 0.20 wt.% KTPClB with a 2:1 molar ratio of ionophore to KTPClB. The Na⁺ sensing membrane consisted of 65.71 wt.% DOS (Bis(2-ethylhexyl) sebacate, Selectophore grade), 32.85 wt.% PVC (Poly(vinyl chloride), Selectophore grade, high molecular weight), 1.00 wt.% Sodium Ionophore X (1.00 %), and 0.44 wt.% NaTFPB with a 2:1 molar ratio of ionophore to NaTFPB. We dissolved all the components of ion-selective membrane (ISM) (total 1.5 g) into 7 mL of THF, stirred the solution for two hours to obtain a homogenous mixture, and poured this mixture into a Petri dish (5 cm diameter), and allowed the THF to evaporate overnight to form the ISM. We then cut the ISM into small circular pieces (\approx 1 cm in diameter), wetted one end of the PVC electrode body (Tygon tubing) with 50 μ L of THF, and pressed the ISM on the wetted area of the tube to seal the end of the tube with the ISM. We filled the tube with 10 mM KCl for the K⁺ ISE and with 10 mM NaCl for the Na⁺ ISE, inserted an AgCl-coated Ag wire in the tube, and sealed the end of the tube with Parafilm. We stored the electrodes in solutions identical to their inner-filling solutions. We prepared the thread-based ISEs (following the procedure described in the manuscript) with the same membrane composition as the conventional ISEs.

Measurements of K⁺ and Na⁺, in Serum and Urine: We poured 20 mL of standard solutions, serum, and urine, in separate beakers. We placed the ISEs selective to K⁺ and Na⁺, and the reference electrode in the solution of serum standard 1, monitored the *emf* values for 2 minutes, removed the electrodes, rinsed them with deionized water, dried them with tissue paper, placed

the ISEs in solution of serum standard 2, and monitored the *emf* values for 2 minutes. We repeated this process for diluted serum standard 3 and serum. We used the *emf* values to obtain a calibration curve and calculate levels of each ion in the serum. We performed this measurement three times for the conventional ISEs (each measurement with a new set of electrodes) and three times for the thread-based ISEs (each measurement with a new set of electrodes).

Figures and Tables

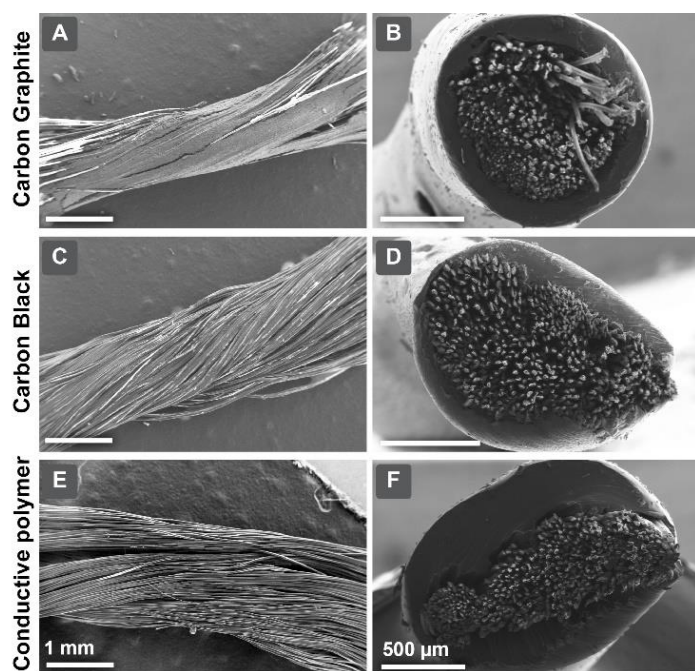


Figure S1. SEM images of Nylon thread coated with inks as labeled in the figure (A, C, E) and coated with the ink and the ISM (B, D, F).

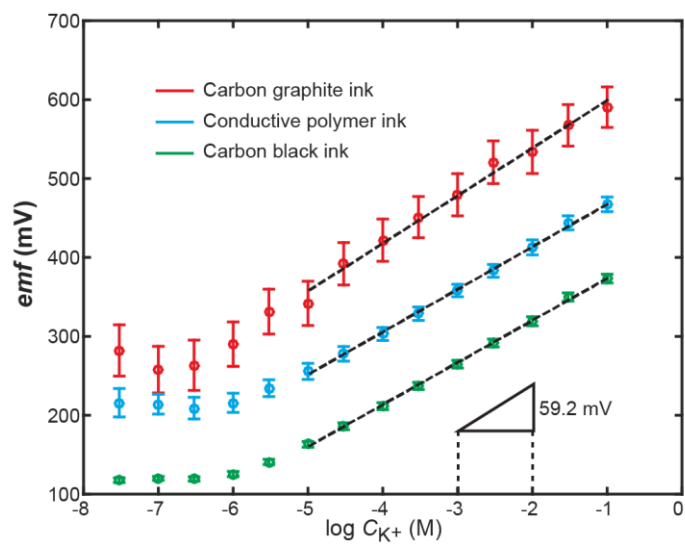


Figure S2. Effect of ion-to-electron transducer material on the response of Nylon-based K^+ sensors.

We show the average and standard deviation of *emf* of five identically-prepared electrodes.

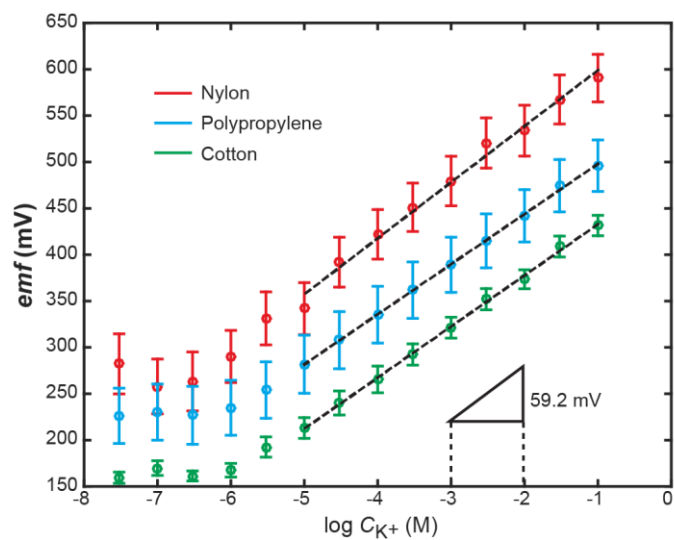


Figure S3. Effect of the material of the thread on the response of K^+ ISEs (with carbon graphite as ion-to-electron transducer material). We placed five identically-prepared ISEs in the test solution, monitored their emf relative to a commercial reference electrode, and changed the concentration of K^+ in the test solution (successive dilutions) to obtain the calibration curves.

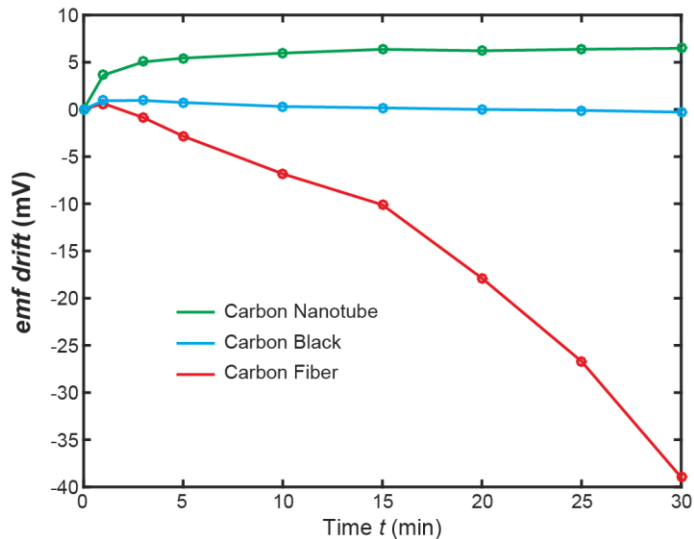


Figure S4. Drift in the emf of K^+ ISEs made with carbon fiber, cotton impregnated with carbon nanotubes, and cotton coated with the carbon black ink. We show the average in emf drift of five identically-prepared electrodes, measured in 100 mM KCl.

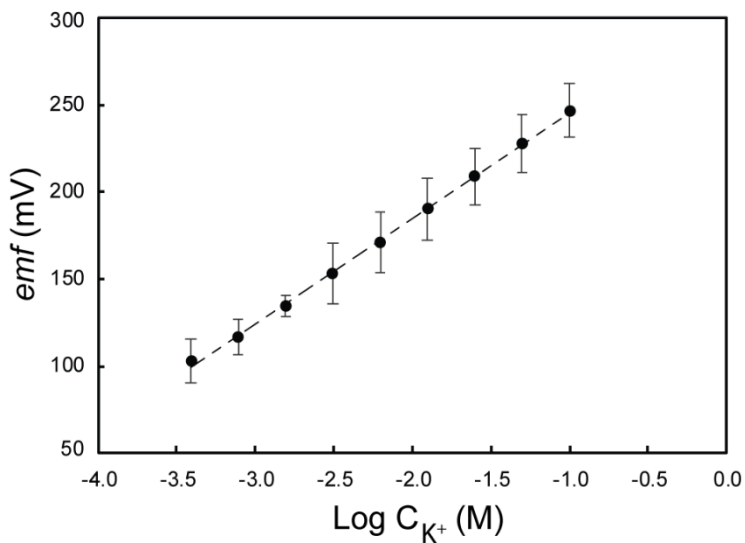


Figure S5. Response of K^+ ISEs made with carbon fiber thread. We show the average and standard deviation of emf of five identically prepared electrodes (slope: 60.6 ± 1.3 mV/decade, E° : 306.2 ± 14.4 mV).

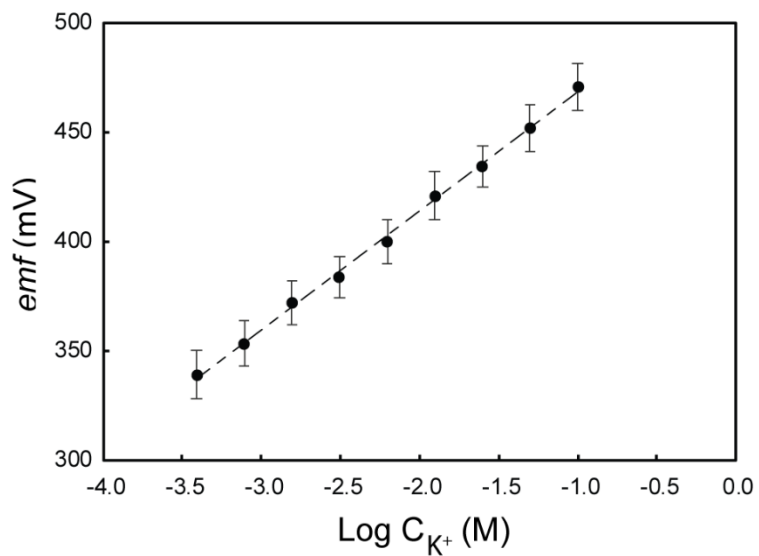


Figure S6. Response of K^+ ISEs made with cotton thread impregnated with carbon nanotubes. We show the average and standard deviation of *emf* of five identically prepared electrodes (slope: 54.5 ± 1.6 mV/decade, E° : 523.4 ± 10.3 mV).

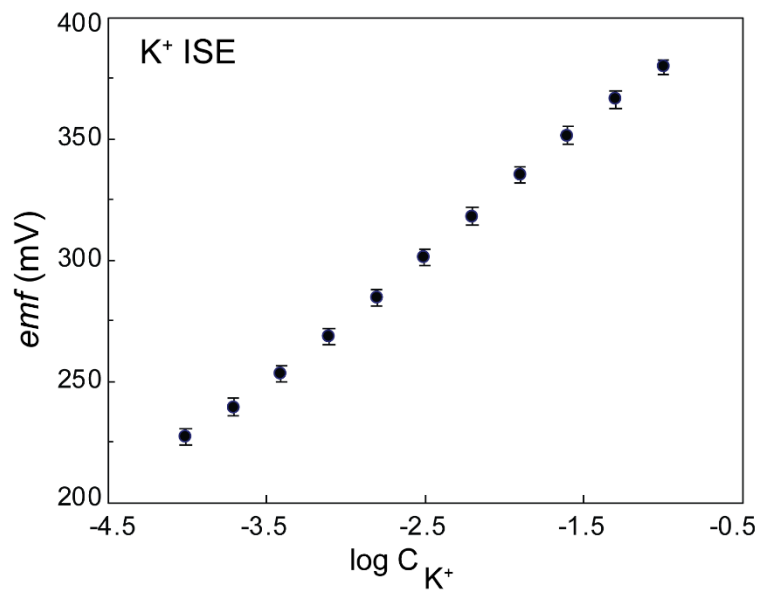


Figure S7. Response of K⁺ ISEs made with cotton and carbon black ink. This response curve is measured four months after fabrication of the sensor. We show the average and standard deviation of *emf* of five identically prepared electrodes (slope: 53.2 ± 0.8 mV/decade, E° : 433.0 ± 3.6 mV). The sensors exhibited an *emf* drift of 0.07 mV/min (measured over 30 minutes in an aqueous 100 mM KCl solution).

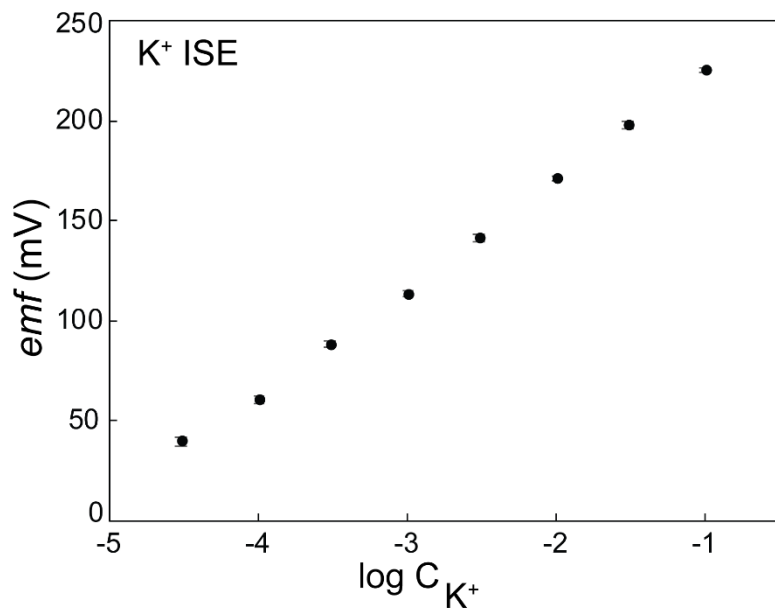


Figure S8. Response of K⁺ ISEs made with cotton and a conductive ink comprised off carbon nanotubes (5 wt.%), PVC (31.67 wt.%), *o*-NPOE (63.3 wt.%). We show the average and standard deviation of *emf* of five identically prepared electrodes (slope: 53.8 ± 0.3 mV/decade, E° : 278.4 ± 1.9 mV). The sensors exhibited an *emf* drift of -0.06 mV/min (measured over 30 minutes in an aqueous 100 mM KCl solution).

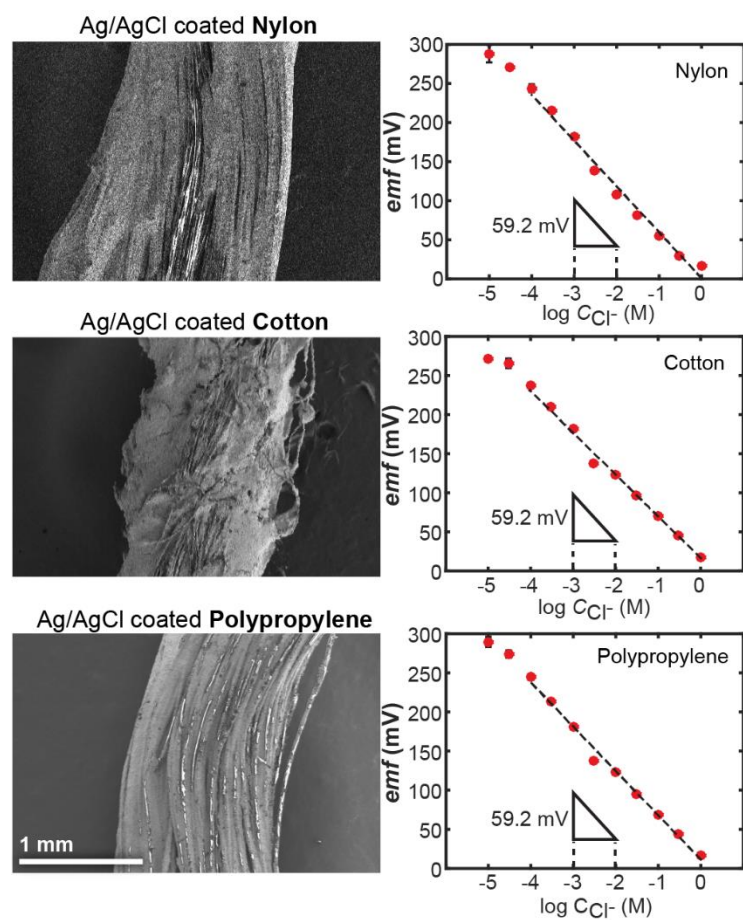


Figure S9. The SEM images of Ag/AgCl coated threads and response of thread-based Cl⁻ sensors made from cotton, polypropylene, and Nylon thread. Error bars (five replicates) are shown, but are mostly concealed by data symbols. Dashed lines show linear fits to the response.

Table S1. Resistance of thread coated with conductive inks.

Type of conductive coating	Thread Type		
	Nylon	Cotton	Polypropylene
Carbon graphite ($\Omega\text{.cm}^{-1}$)	95.4 ± 22.4	169.5 ± 64.8	114.1 ± 22.8
Carbon black ($\text{k}\Omega\text{.cm}^{-1}$)	4.1 ± 0.2	3.3 ± 0.9	—
PEDOT:PSS ($\Omega\text{.cm}^{-1}$)	209.0 ± 15.2	—	—
Ag/AgCl ($\Omega\text{.cm}^{-1}$)	2.5 ± 0.6	0.3 ± 0.1	2.32 ± 1.4

Table S2. Resistance of thread coated with conductive inks and ISM.

Ion-to-electron transducer material and ISM	Thread Type		
	Nylon	Cotton	Polypropylene
Carbon graphite, K ⁺ ISM (kΩ)	185.1 ± 28.1	286.9 ± 65.1	275.9 ± 90.7
Carbon black, K ⁺ ISM (kΩ)	143.1 ± 43.1	178.4 ± 38.5	—
PEDOT:PSS, K ⁺ ISM (kΩ)	145.2 ± 60.3	—	—

Table S3. The concentration range of physiological ions in blood of healthy individuals and the tolerable error in the measurement of ion concentrations enforced by U.S. Federal Regulations.¹⁵

	Normal Range	Tolerable error in the analysis of ion concentrations enforced by U.S. Federal Regulations ¹⁵
Na ⁺	135–150 mM	4.0 mM
K ⁺	3.5–5.0 mM	0.5 mM
Cl ⁻	98–108 mM	5%

Table S4. Concentration of chloride in aqueous solutions in contact with sand and soil determined by the thread-based Cl⁻ sensor. We calculated the error as $(C_{\text{determined}} - C_{\text{known}}) / C_{\text{known}}$.

	Thread-based Cl ⁻ Sensor	
	Concentration (mg/L)	Percent Error
Sand in contact with 100 mM (3500 mg/L) Cl ⁻ (aq)	3479 ± 99	-2.0
Sand in contact with 10 mM (350 mg/L) Cl ⁻ (aq)	359 ± 23	2.5
Sand in contact with 1 mM (35 mg/L) Cl ⁻ (aq)	38 ± 7	8.5
Soil in contact with 100 mM (3500 mg/L) Cl ⁻ (aq)	3452 ± 90	-1.3
Soil in contact with 10 mM (350 mg/L) Cl ⁻ (aq)	348 ± 12	-1.9
Soil in contact with 1 mM (35 mg/L) Cl ⁻ (aq)	36.4 ± 11	4.0
Sand in contact with unknown amount of Cl ⁻ (aq)	1495 ± 55	-2.9*
Soil in contact with unknown amount of Cl ⁻ (aq)	221 ± 13	3.7*

* True concentration of Cl⁻ was determined by a commercial chloride test strip (Hach Chloride QuanTab)

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