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Self-Powered Potentiometric Sensor Transduction to a Capacitive Electronic Component for Later Readout

Sunil Kumar Sailapu, Pitchnaree Kraikaew, Neus Sabaté,* and Eric Bakker*

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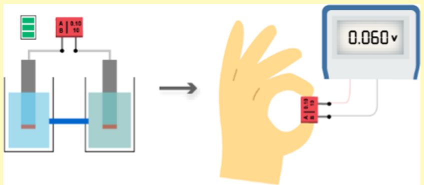
ABSTRACT: Potentiometric sensors operate as galvanic cells where the voltage is spontaneously generated as a function of the sample composition. We show here that energy can be harvested, stored during the sensing process without external power, and physically isolated from the sensor circuit for later readout. This is accomplished by placing an electronic capacitor as a portable transduction component between the indicator and the reference electrode at the point where one would ordinarily connect the high-input-impedance voltmeter. The voltage across this isolated capacitor indicates the originally measured ion activity and can be read out conveniently, for example, using a simple handheld multimeter. The capacitor is shown to maintain the transferred charge for hours after its complete disconnection from the sensor. The concept is demonstrated to detect the physiological concentrations of K^+ in artificial sweat samples. The methodology provides a readout principle that could become very useful in portable form factors and opens possibilities for potentiometric detection in point-of-care applications and inexpensive sensing devices where an external power source is not desired.



KEYWORDS: *self-powered sensor, potentiometry, electrochemical energy transfer, capacitor, ionophore*

Chemical sensors are increasingly being adapted and developed for successful deployment in implantable and wearable devices,[1,2] as well as environmental monitors.[3,4] However, an issue of key importance with these applications is the power supply, where the energy autonomy of sensing devices is identified as an important enabling characteristic.[5] Sustainable power sources should be able to harvest energy from the environment (light, heat, and movement) or from the sample itself.[6,7] Self-powered sensors are one advanced avenue toward achieving device power autonomy. In a self-powered electrochemical sensor, the amount of harvested energy from the sample contains the requested information about a physical or chemical parameter. This allows one to merge the power source and the sensor into a single element that may more easily become autonomous.[8−10]

So far, the field of self-powered chemical sensors has predominantly relied on biofuel cells where enzymes or bacteria oxidize or reduce a compound at a sensing electrode that is combined with a second electrode to yield a galvanic cell.[11,12] This approach has led to self-powered versions of a wide range of amperometric sensors,[13,14] resulting in a proliferation of the associated literature in recent years.

Potentiometric sensing probes are widely established for the measurement of a variety of important parameters, including pH.[15−17] The measurement is intrinsically low power because it involves a readout of a potential that is spontaneously generated by the electrochemical cell. A battery-free ion-sensing patch has recently demonstrated detection of Na^+ ions based on this potential measurement.[18] However, because such probes are read out under zero-current conditions, it may appear unrealistic that a response could be realized in the form of energy that could be harvested and stored during the sensing process.

Fortunately, recent work has introduced new ways of reading out potentiometric sensing probes that may help design self-powered potentiometric systems. One of them involves a capacitive element placed in series with the indicator electrode that accumulates charge once the sensor deviates from zero-current conditions.[19] Here, the change in cell potential during the measurement results in a small transient current excursion before settling to a new electrochemical equilibrium state. Using capacitive conducting polymers in combination with a constant applied cell potential, Bobacka's group introduced this principle to show that the accumulated charge relates selectively to the ion activity change in sample.[20−22] Very recently, our group further extended this approach using an external electronic capacitor instead of a polymer film, demonstrating an unsurpassed precision of pH measurements in seawater as a model example.[23] We note, however, that these strategies rely on the application of an external potential and are therefore not yet self-powered. A conceptually similar approach allowed for a colorimetric readout by placing a redox indicator in a bipolar electrode

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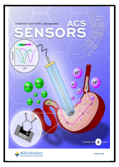

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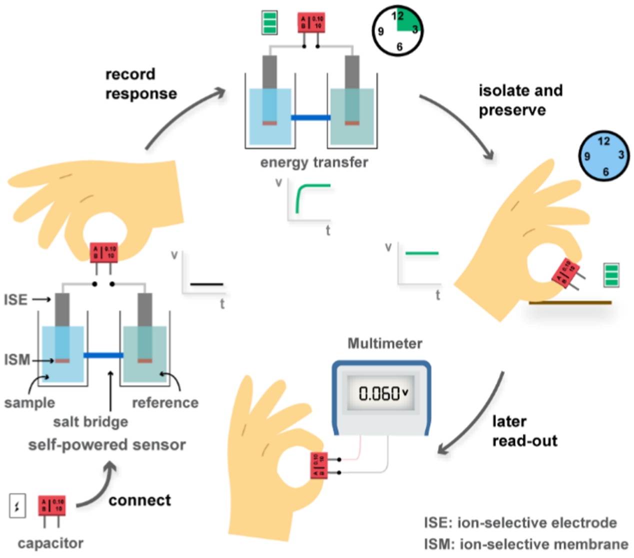
arrangement,[24] where the tolerable charge passed to avoid undesired potential perturbations was also characterized.

In this work, a potentiometric sensor is read out by interfacing it with a capacitor to harvest and store energy as a result of the transient current flow. It involves a closed circuit where the potential change between the indicator and the reference electrode, brought about selectively by the sample composition change, is directly transferred onto the capacitor to keep the overall potential difference of the closed loop zero. In this way, the energy stored in the capacitor can be directly related to the ion activity change, forming the basis for a self-powered potentiometric system. This approach allows a later voltage readout of the isolated capacitor using a simple handheld multimeter, as the stored energy remains unaffected even after disconnecting the sensing probes (see Scheme 1).

Scheme 1. Schematic Illustration of the Technique used to Preserve Ion Activity Response in a Capacitor for an Isolated Storage and Later Readout



As a result, the acquisition of sensor response is possible without requiring a high input impedance instrument. In this way, a portable response carrying transduction/information storage element (capacitor) akin to a strip-based optical readout becomes achievable. The approach may lay the groundwork for a new generation of self-powered potentiometric devices that could operate in a standalone manner using the energy harvested during the sensing process. The approach is demonstrated here with the detection of the physiological concentration of K^+ ions in an artificial sweat sample as a model example of practical relevance.

■ EXPERIMENTAL SECTION

Materials. Potassium chloride (KCl), agarose (Type 1, low EEO), valinomycin (potassium ionophore I), poly(vinyl chloride) (PVC, high molecular weight), 2-nitrophenyloctylether (*o*-NPOE), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), tetrakis(4-chlorophenyl)borate tetradodecylammonium salt (ETH 500), tetrahydrofuran (THF), sodium chloride (NaCl), ammonium hydroxide, lithium acetate dihydrate, and hydrochloric acid (HCl) were obtained from Sigma-Aldrich.

Urea (Merck), lactic acid (90%, Fluka), potassium nitrate (KNO_3, Thermo Fisher Scientific) were used as purchased without any modifications. Deionized water (resistivity > 18 MΩ cm) at room temperature was used in all the experiments. Metallized polyester poly(ethylene terephthalate) (PET) capacitors (Wima) of different values were obtained from Distrelec, Switzerland.

Sample Preparation. KCl solution, with and without a 1 mM KNO_3 background solution, was prepared by dissolving the respective salts in deionized water.

The artificial sweat was prepared according to the DIN 53160-2 standard as follows. Urea (0.5 g), NaCl (2.5 g), and lactic acid (0.5 g) were dissolved in 450 mL of water. The pH of this solution was subsequently adjusted to 6.5 using 1% NH_4OH. The volume of this solution was then made up to 500 mL by adding deionized water. A defined amount of K^+ ions was introduced into this artificial sweat for potassium sensing using the self-powered sensor.

Preparation of Electrodes and a Salt Bridge. A double-junction Ag/AgCl electrode (3 M KCl/1 M LiOAc) and a Pt electrode were procured from Metrohm, Switzerland and used as the reference and counter electrodes, respectively.

Ag/AgCl electrodes were prepared through electrochemical oxidation of a Ag electrode tip (of diameter 3 mm, order no. 6.1204.330, Metrohm, Switzerland) in a solution of 1 M HCl for 10 min at a constant anodic current of 1 mA/cm^2. These coated electrodes were washed with deionized water before use.

K^+-ISEs were prepared by placing a K^+-selective membrane in an ion-selective electrode (ISE) body (Oesch Sensor Technology, Sargans, Switzerland). The membrane was prepared from a mixture composed of 58.36 mg of PVC, 116.73 mg of *o*-NPOE, 0.90 mg of KTFPB, and 3.33 mg of valinomycin. To this mixture, 20.67 mg of ETH 500 was added to reduce membrane resistance and improve ion selectivity.[21,24] This mixture was dissolved in 2 mL of THF before casting into a glass ring (of inner diameter 22 mm) affixed to a glass slide. The solution was left undisturbed overnight at room temperature to allow the solvent to evaporate and form a membrane. The acquired membrane was cut into circular pieces (of diameter 8 mm) with a hole puncher. The cut membrane pieces were placed in an ISE body with an inner filling solution of 1 mM KCl. These K^+-ISEs were left conditioned in a 1 mM KCl solution overnight.

The salt bridge for two compartment-based experiments was prepared using a 21 cm long U-shaped hollow PVC tube (of inner diameter 1.6 mm). The tube was loaded with 1% agarose gel containing a 1 M KNO_3 solution. For experiments with the K^+-ISE, 1 M KNO_3 was replaced with 1 M LiOAc.

Self-Powered Sensor. For construction of the self-powered sensor, a beaker containing 50 mL of 1 mM KCl solution served as the reference compartment, while another beaker containing 50 mL of the investigated sample was chosen as the sample compartment. The specific sample compositions are mentioned at the specific location in the text. The ionic connection between the compartments (beakers) was established using a salt bridge, while the electrochemical cell was completed by immersing otherwise identical indicator and reference elements into each solution. These electrodes were either Ag/AgCl electrodes or K^+-ISEs depending on the experiment and mentioned where appropriate.

Sensing Measurements. The concentration of the solution in the reference compartment was kept constant. The open- and closed-circuit voltage measurements of the sensor were carried out with the EMF16 data acquisition system (input impedance of $\sim 10^{13}$ Ω; Lawson Labs, Inc., Malvern, PA) by making small concentration changes in the solution contained in the sample compartment.

Dual in-line package (DIP) switches were used to make and break the connection between the capacitor and the sensor. The capacitor was connected to the sensor, and a concentration change was made in the solution contained in the sample compartment. After a specific time (1 min for Ag/AgCl electrodes; 5 min for ISEs), the connection between the capacitor and the sensor was broken. The voltage across the capacitor was then measured with either a Keithley 2000 benchtop digital multimeter (input resistance > 10 GΩ) or a Peak Tech 3430 handheld multimeter (input resistance of 9 MΩ). However, in experiments related to the time-dependent study of the capacitor voltage, the disconnected capacitor was left isolated in the open air for 24 h before making a voltage measurement.

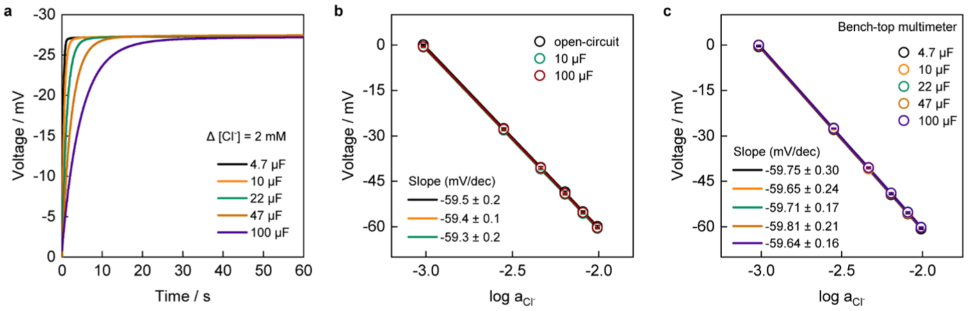


Figure 1. (a) Evolution of voltages across different values of the capacitor connected to a self-powered sensor for detection of a 2 mM concentration change in the Cl^- ion ($\Delta[Cl^-] = 2$ mM; sample compartment: 3 mM KCl; reference compartment: 1 mM KCl). (b) Voltage responses for Cl^- ion activities in the KCl solution measured with and without the capacitor connected to the sensor using a high input impedance data acquisition system (EMF16, Lawson Labs). (c) Voltage responses for Cl^- ion activities in the KCl solution obtained from capacitor voltages measured with a benchtop multimeter (Keithley 2000), immediately after disconnecting it from the sensor. The values in (b, c) are represented as an average with standard deviation from three independent experiments. The solid line represents the linear regression fit for the average values.

RESULTS AND DISCUSSION

The methodology involved in ion detection with potentiometric probes through the readout of an isolated charged capacitor is shown in Scheme 1. The sensor is constructed with two identical ISEs placed in different compartments that are connected by a salt bridge. The sample compartment contains a variable concentration of the analyte ion, while the composition of the reference compartment is kept constant. The self-powered sensor resembles the configuration of an electrolyte concentration cell, and the open-circuit potential difference (E_{cell}) between the two ISEs in the sample and reference compartments can be expressed as

$$E_{\text{cell}} = \frac{s}{z} \log \frac{a_{\text{sample}}}{a_{\text{reference}}} \tag{1}$$

where s is the Nernstian slope, z is the charge of the analyte ion (positive for cations), and a denotes the ion activity in solution. Here, the energy for the spontaneous potential response according to eq 1 is transferred to a capacitor by connecting it across the electrode terminals. Because the algebraic sum of the potential differences of the closed circuit is now zero, the potential drop over the capacitor, E_C, compensates the original cell potential expressed in eq 1

$$E_c = \frac{1}{C} \int i \, dt = \frac{Q}{C} = \frac{s}{z} \log \frac{a_{\text{sample}}}{a_{\text{reference}}} \tag{2}$$

where E_c is the potential across the sensor terminals when the circuit is closed, C is the capacitance of the capacitor, and i is the current flowing through the closed circuit over time t during the charging process, resulting in a charge Q. Subsequently, the energy transferred to the capacitor is preserved by physically isolating it from the sensor for a later readout as desired, for example, by a simple handheld multimeter.

To investigate the influence of an external capacitor interfaced with a self-powered sensor, two Ag/AgCl electrodes were initially employed as the indicator and reference probes for detection of Cl^- ions in the KCl solution as a model system. The response of these probes was evaluated individually against a double-junction Ag/AgCl (3 M KCl/1 M LiOAc) electrode and confirmed to exhibit a Nernstian response in the ion activity range (1−10 mM) of interest (Figure S1). A self-powered sensor was then developed by introducing these probes in separate compartments (reference and sample) connected via a gel-based KNO_3 salt bridge. The KNO_3 salt bridge was used, as it does not interfere with Cl^- ion detection and due to the comparable size and mobility of the NO_3^- ion (to Cl^- ion). The KCl concentration in both compartments was initially kept at 1 mM (equilibrium situation) for the initial electrochemical potential across the probes to be near zero. A Nernstian behavior for chloride with a lower detection limit of 25 μM was confirmed without (Figure S2) and with a 1 mM KNO_3 background solution (Figure S3).

When a capacitor was introduced between the electrodes, a sustained potential developed across it over time after a concentration change in the sample compartment. For the capacitors tested (1−100 μF), the charging time of the capacitor increased with increasing capacitance value, as shown in Figure 1a, but the stabilized voltage readings recorded across the connected capacitor revealed the same Nernstian response as when no capacitor was present (Figure 1b). The capacitor voltage achieved ∼99% of the open-circuit potential (E_{cell}) within 30 s (for capacitance below 100 μF) after an ion concentration change, but the readings were acquired after 1 min to assure maximum energy transfer. The capacitor voltage is stable near the open-circuit potential with less than 0.5 mV change for at least 60 s (Figure S4). We used a symmetric system, as it initially provides a zero voltage across the electrodes. However, the above-demonstrated phenomena work even if the initial concentrations in both compartments are not equal (Figure S5).

Neither the final potential value nor the Nernstian behavior of the potentiometric sensing system is substantially altered by the introduction of a capacitor. Possible deviations are expected for solution compartments lacking the required ion capacity (quantity) to pass the necessary charge across the cell without being perturbed. This can be estimated from eq 2 in combination with Faraday's law

$$\Delta n = -\frac{C}{F} \frac{s}{z} \log \frac{a_{\text{sample}}}{a_{\text{reference}}} \tag{3}$$

where F is Faraday's constant. For a 10-fold activity change (59.2 mV for a monovalent ion) and a 100 μF capacitor, $\Delta n = 6 \times 10^{-11}$ mol. If the allowable quantity perturbation is 1%, a lower concentration of 1 mM should translate into a minimum sample volume of just 0.6 nL. It can therefore be assumed that the sensor response can be accurately recorded by a capacitive

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element in the form of energy in most cases of practical relevance.

The possibility to preserve and read out this transferred energy by disassociating the capacitor completely from the self-powered sensor was further investigated. Here, the capacitor was initially connected to the self-powered sensor, and the solution concentration in the sample compartment altered to induce a potential difference across the electrodes to charge the capacitor. After the same waiting time of 1 min, the capacitor was disconnected from the sensor and the potential across it was recorded with a benchtop multimeter. Figure 1c indicates that the observed capacitor voltages correspond to the open-circuit potentials and a Nernstian behavior is observed for capacitances in the range 1−100 μF. Moreover, the response voltage can be extracted from the same sensor repeatedly by physically reintroducing the capacitor. This is demonstrated in Figure 2a, where a capacitor was charged, disconnected, and then reconnected after complete discharge, for a total of 10 cycles. The voltage readings remained the same upon reconnecting it to the self-powered sensor (−61.03 ± 0.04 mV, see Figure S6). The energy can be transferred multiple times without affecting the original response. As the capacitor voltages are in the range of mV, the measurements can also be performed by a simple, inexpensive handheld multimeter, as confirmed by the data in Figure 2b. ISEs typically require a high input impedance potentiometer to avoid stray currents during measurements. While the methodology introduced here requires a transient current to charge the capacitor, the final measurement of the capacitor voltage itself no longer involves a high-resistance circuit and can be performed with less complex instrumentation.

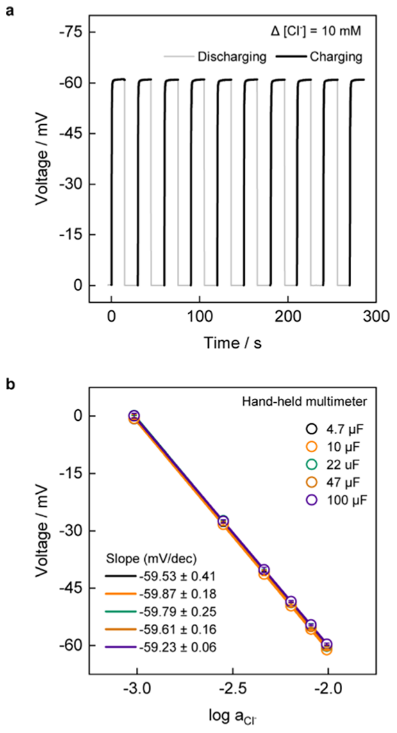

Figure 2. (a) Repetitive voltage measurements made on the same sensor by connecting a discharged capacitor (10 μF) for 10 cycles (Δ[Cl⁻] = 10 mM; sample compartment: 11 mM KCl; reference compartment: 1 mM KCl). (b) Voltage responses for Cl⁻ ion activities in the KCl solution obtained from capacitor voltages measured with a handheld multimeter (Peak Tech 3440), immediately following its disconnection from the sensor. The values are represented as an average with standard deviation from three independent experiments. The solid line represents the linear regression fit for the obtained values.

The ability to preserve the energy for a specific time to enable prospects of a later readout was further investigated. Generally, it is dangerous and not recommended to physically connect/disconnect a capacitor if a high voltage/current/charge is associated with it (hundreds of volts and tens of amperes) due to the possibility of an electric shock. However, in the present case, the magnitudes of electrical parameters are significantly lower (mV, μA). Therefore, the capacitor can be disconnected physically, as shown in Scheme 1, by holding their electrically insulated body and strictly avoiding any contact with the terminals. The responses from different capacitors kept in isolation for 24 h after disconnecting it from the self-powered sensor are shown in Figure 3a. The voltages persisted across the capacitors even 24 h after isolating them from the sensing circuit. The responses remained close to Nernstian for capacitances above 4.7 μF, and the deviation of the slope along with the error in its estimate reduced for higher capacitance values due to a slower self-discharge rate. A closer inspection of the measured voltage gave changes expressed as $\Delta V_t = V_{\text{charged}} - V_{24\text{ h}}$ from the charged value, when in contact with the sensing circuit. As shown in Figure 3b, the voltage drop due to self-discharge is below 0.5 mV for capacitances above 4.7 μF. This drop decreased with increasing capacitance.

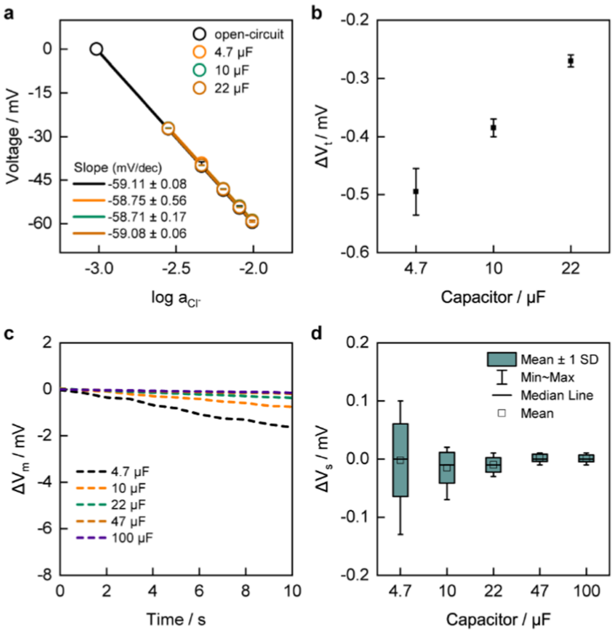

Figure 3. (a) Voltage responses to Cl⁻ ion activities in KCl solution obtained from the measured capacitor voltages after isolating it from the sensor for 24 h. The potentiometric measurement involving no capacitor is shown for reference. (b) Voltage losses observed with different charged capacitors after 24 h isolation from the sensor. The values in (a, b) are represented as an average with standard deviation from three independent experiments. The solid line in (a) indicates the linear regression fit for the average values. (c) Magnitude of voltage change across isolated capacitor over time, while measuring with a handheld multimeter. (d) Magnitude of variation caused in capacitor voltage due to the switching action. The displayed statistical information is obtained from the analysis of 15 measurements.

The results indicate that the charged capacitor can be isolated from the sensor and stored for at least 24 h before measuring the voltage with a simple handheld multimeter, within the indicated error.

During the readout process with a handheld multimeter, the capacitor slowly discharges (Figure 3c). At a given internal resistance of the multimeter, smaller capacitances with values like 4.7 μF give a decreased discharge time constant and a higher voltage decay rate. For a capacitance of 10 μF or above, the voltage drop ($\Delta V_m = V_{\text{initial}} - V_t$; $V_{\text{initial}} = -28$ mV) is less than 0.12 mV during the first 2 s, 0.40 mV for 5 s, and 0.80 mV for 10 s. The corresponding measurements for different capacitors are shown in Table S1. Further, the deviation in capacitor voltage (ΔV_s) caused upon disconnection (switching) from the value while in contact with the sensor circuit was also slightly larger with lesser capacitances, but remained within ±0.1 mV (Figure 3d). Considering the data in relation to Figure 3, it seems advantageous to use a capacitor of a value greater than 10 μF.

The methodology was examined with ISEs to assess its applicability to real-life samples, and K^+-ISEs featuring a valinomycin-based ion-selective membrane (ISM) were explored for this purpose. A Nernstian response was obtained with the prepared K^+-ISEs when evaluated individually against a conventional double-junction reference electrode (Figure S7). These ISEs were then incorporated in a symmetrical sensing circuit, in complete analogy to the Ag/AgCl elements discussed above. Here, the KNO_3 salt bridge was replaced with a gel-based LiOAc salt bridge to avoid any interference from K^+ ions. The ISEs again gave a Nernstian response for K^+-ion activities and exhibited a lower detection limit of 10 μM (Figure S8). The response of the self-powered sensor containing K^+-ISEs upon introduction of the capacitor between the probe terminals is shown in Figure 4a. While the smaller capacitance values gave a desired Nernstian response to ion activities, a deviation from this behavior was observed at capacitance values of 47 μF and higher (Figure S9). This is attributed to the increasing charge passing through the polymeric membrane as characterized earlier by controlled current experiments.[24] Excessive current transients give rise to deviations from the Nernstian behavior. For this reason, the use of capacitances with values between 10 and 22 μF appears optimal for the conditions used here.

A capacitor of 10 μF was applied to demonstrate the analysis of potassium-spiked artificial sweat samples with K^+-ISEs in the physiologically relevant concentration range (Figure 4b). In analogy to above, the sample compartment contained the variable artificial sweat, while the reference compartment contained 1 mM KCl. The connected 10 μF capacitor was disconnected after getting charged by the self-powered sensor due to these introduced concentration changes. The isolated capacitor read by a handheld multimeter gave a response with a near-Nernstian response slope (56.28 ± 0.33 mV). The corresponding measurement made using a 22 μF capacitor gave a similar result (56.20 ± 0.16 mV).

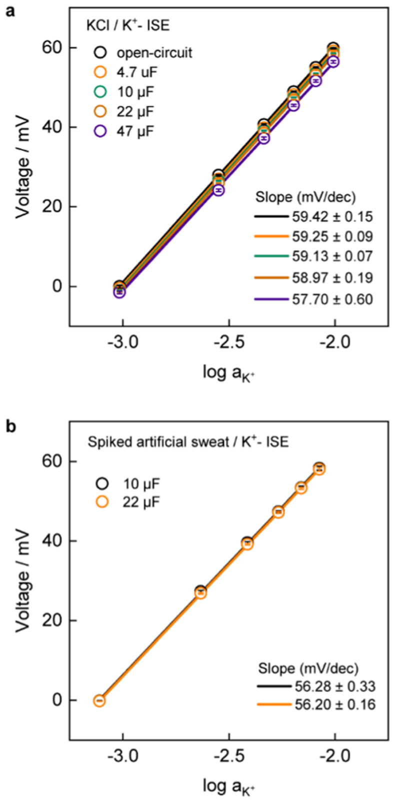

Figure 4. Voltage responses for K^+-ion activity in (a) KCl solution obtained with the capacitor connected to the sensor, (b) artificial sweat solutions obtained by measuring the capacitor voltages with a handheld multimeter after 24 h of its isolation from the sensor. The readings are represented as an average with standard deviation from three independent experiments. The solid line represents the linear regression fit for the average values.

■ CONCLUSIONS

A novel self-powered measuring strategy that involves an extremely simple closed-circuit electrode setup and an electronic capacitor has been presented. The method proposes to capture the transient current that is produced upon the building-up of a potential response in a potentiometric sensor by preserving the accumulated charge in the capacitor. This capacitor assumes the role of the transduction element of the sensor to selectively detect physiological concentrations of K^+ ions in an artificial sweat medium. Interestingly, the response of the sensor can be conserved in the capacitor in the form of energy for many hours after its complete isolation from the sensor. Depending on the magnitude of the capacitance value used, the capacitor charging time and charge storage ability can be conveniently adapted without affecting the sensor response. In fact, the flexibility of the readout methodology allows a repeated readout of the same sample.

The ability to preserve the response in a portable capacitor with complete isolation from the sensor alleviates the need for high-input-impedance-based complex instrumentation and makes the analysis possible using a simple handheld multimeter. For this, one should avoid very high resistance ion-selective membranes to avoid excessive RC time constants and adverse polarization effects, which were however not problematic with the ionophore-based plasticized PVC membranes used here. Additionally, the energy stored in the capacitor could further be utilized. We anticipate that the readout strategy presented in this work expands the scope of ion-to-electron transduction-based self-powered sensors for point-of-care applications. It may form the basis to realize a potentiometric sensing device fully driven by the energy harvested during the sensing process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssensors.0c01284.

> Voltage response of Ag/AgCl electrodes and ISEs measured against a conventional double-junction reference electrode; voltage response in the presence of a background solution; detection limit measurements; and voltage measurements across the capacitor (PDF)

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Author Contributions

S.K.S. and P.K. contributed equally to this work. S.K.S., N.S., and E.B. conceived the idea. S.K.S., P.K., and E.B. designed the experiments. S.K.S. and P.K. performed the experiments. S.K.S., P.K., and E.B. analyzed the data. S.K.S., N.S., and E.B. wrote the paper.

Notes

The authors declare no competing financial interest.

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