MULTIPLEXED, SELF-CALIBRATED POTENTIOMETRIC SENSOR SYSTEM FOR LONG-TERM, IN SITU MEASUREMENTS

Zhehao Zhang, Elena Boselli and Ian Papautsky*

Department of Biomedical Engineering, University of Illinois Chicago, Chicago, IL 60607, USA

ABSTRACT

We developed a potentiometric sensor system that includes a portable device and a multiplexed sensor based on solid-contact ion-selective electrodes (SCISE). SCISEs are fabricated using printed circuit board (PCB) and mesoporous carbon black (MCB) as the ion-to-electron transducer. The device supports sensor readout as well as automated sensor calibration, making it suitable for long term, *in situ* measurements.

KEYWORDS: Ion-selective electrode, printed circuit board, *in situ* measurements

INTRODUCTION

Potentiometric sensors are commonly applied to point-of-care testing, wearables, and environmental monitoring [1,2]. Miniaturization of sensors often relies on microfabrication and metal evaporation technologies. Here, we fabricated miniaturized sensors using PCB technology as an alternative method, which can be advantageous in terms of cost and scalability. On the system level, we built an electromechanical device that not only does sensor readout and wireless data transmission, but also performs automatic on-site calibration. The latter is particularly important to correct for variations in sensor stability and reproducibility in the long term, and to enable the system to be deployed autonomously in the field.

EXPERIMENTAL

SCISEs for K^+ and NO_3^- ions are fabricated based on the standard PCB process. Solid contact layer (MCB) and ion-selective membranes were formed by drop casting using adhesives as guidance (Figure 1A) [3]. To increase stability, the sensor membranes were cast at an offset position laterally from the underlying layers. A Ag/AgCl reference electrode was fabricated by electroplating silver followed by electro-chloridization. The sensor was enclosed in a straight microchannel (17 mm × 2.5 mm × 0.17 mm) constructed using a hybrid structure of PSA tape and 3D printing. The readout device was based on a custom circuit produced by following the standard PCB workflow (Figure 1B). The circuit reads sensor via USB and an analog front end (buffer+ADC). The circuit features dc-dc boost converters and motor driver to actuate miniature solenoid valves (V1, V2) and peristaltic pump (P). Programming and wireless transmission were done on a microcontroller (MCU) housed separately on Arduino. The device is packaged in a 3D printed enclosure and is powered by battery (Figure 1C).

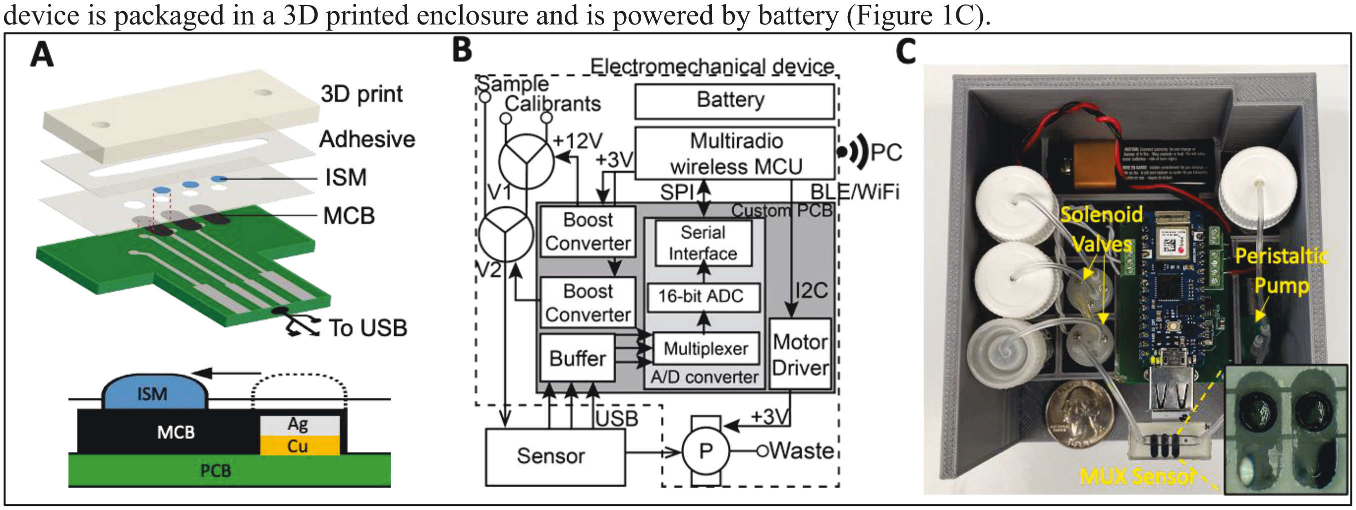

Figure 1: Potentiometric sensor system for in situ measurements. The system consists of a multiplexed ISE sensor and an electromechanical device for sensor readout and calibration. (A-top) Explosive view of the sensor enclosed in a microfluidic channel; (A-bottom) cross-section of sensor showing lateral displacement of ion-selective membrane. (B) System block diagram. (C) Photograph of the assembled system.

RESULTS AND DISCUSSION

The sensors showed near-Nernstian response (56.6/-57.4 mV/dec for K^+ and NO_3^-, respectively), and micromolar detection limits (1.9/3.6 μM) in the microchannel (Figure 2A). In the long term, the sensors have maintained most of their sensitivity (>90%) and selectivity ($logP_{K+,Na+} \leq -3.72$, $logP_{NO3-,Cl-} = -2.44$) over 3 weeks (Figure 2B). Baseline drift was ~2 mV/day, suggesting that single-point calibration should suffice when the sensor was used on daily basis. The capability of the sensor system was demonstrated in automated nutrient analyses in xylem sap of corn plants (*Zea mays*), where the sensor showed stable and reproducible response during repetitive measurements (Figure 2C). The results showed strong correlation (R^2>0.91) with commercial ISEs (Figure 2D).

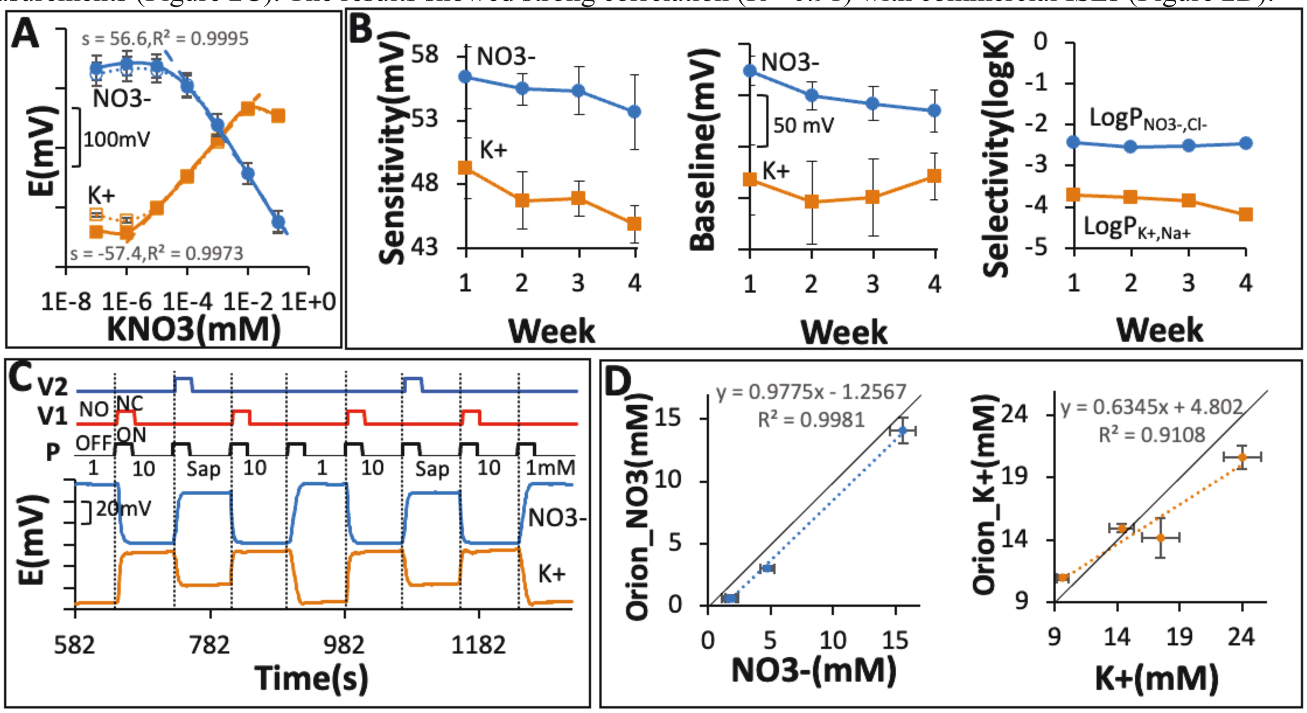

Figure 2: Sensor performance. (A) Calibrations of ISEs (n=3) under flow (solid lines) and static (dashed lines) conditions. (B) (left to right) Sensitivity, baseline (at 1 mM KNO3) and selectivity of ISEs(n=3-8) over 3 weeks. Sensors were stored dry in air between measurements. (C) Corn plant xylem sap test with programmed measurement sequence. The sensors were calibrated before and after each sap measurement with KNO_3(1-10mM)+NaCl. (D) Comparison of ion concentrations in xylem sap between our sensors and commercial ISEs (Orion).

CONCLUSION

Using PCB technology, we successfully fabricated miniaturized SCISE sensors and integrated them with a electromechanical system for measurements in the field. The sensor system is multiplexed, portable, cost-effective, and supports auto-calibration during long-term, *in situ* measurements. We expect the device to be useful in a variety of applications in biomedical, environmental, and geochemical analyses.

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REFERENCES

[1] E. Zdrachek and E. Bakker, *Anal. Chem.*, 2021, 93, 72-102.
[2] Y. Shao, Y. Ying and J. Ping, *Chem. Soc. Rev.*, 2020, 49, 4405-4465.
[3] Z. Zhang and I. Papautsky, *Electroanalysis*, 2022, (doi:10.1002/elan.202100686).

CONTACT

* Ian Papautsky; +1-312-413-3800; papauts@uic.edu