MULTIPLEX SENSOR FOR ION SENSING BASED ON PRINTED CIRCUIT BOARD

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ABSTRACT

We fabricated and evaluated multiplexed ion-selective electrodes (ISEs) by modifying printed circuit board (PCB). The multiplexed sensor consisted of all-solid-state K^+ and NO_3^- ISEs, together with a Ag/AgCl reference. The sensor was further embedded in a microfluidic microchannel for in-line continuous analysis, and was characterized for up to one week of operation. Both ISEs showed a near-Nernstian response (~52 mV/dec) and reasonable stabilities (baseline drift ~2.9 mV/day). The sensor provides a versatile and low-cost tool for monitoring concentrations of different ions in many biomedical, environmental and agricultural applications.

KEYWORDS: Ion-selective electrode (ISE), Printed circuit board (PCB), Potentiometric sensor

INTRODUCTION

Combining electrochemical sensors with microfluidics presents an attractive approach for *in situ* measurements in point-of-care testing, wearable devices and lab-on-chip systems.[1] One class of such sensors are based on ion-selective electrodes (ISEs), which are potentiometric sensors that measure activities of ions. Compared to other electrochemical methods, such as stripping voltammetry or ISFETs, they are simpler in design and easier to use. Thus, they are particularly well suited for *in situ* applications in wearable or point-of-care sensing.

All-solid-state ISEs differ from conventional ISEs in that the inner filling solution is replaced by a solid contact material.[2-3] The removal of liquid compartment can make the sensor more durable and flexible, and also easier to miniaturize. Here we explore PCB as a platform to multiplex all-solid-state ISEs for different ions. PCB has previously been used to construct multiplexed ISEs and successfully applied to monitoring ion fluxes in cell culture.[4] The standardized PCB technology enables fast prototyping of sensors and can also be cost-effective during mass production.

EXPERIMENTAL

The multiplex sensors were fabricated from double-sided PCBs, where the top side was used to laminate sensing layers and the bottom side was used for electrical conduction and they were interconnected through the via structure (Figure 1A). Graphitized mesoporous carbon was used as the solid contact for ISEs. The solid contact layer and the ion-selective membranes were subsequently coated onto PCB by drop-casting. The membranes were based on ion-exchangers (tetrakis(4-chlorophenyl)-borate for K^+, tridodecylmethylammonium for NO_3^-) without ionophores. Adhesive transfer tapes were used to pattern sensing layers, which resulted ISEs of 1.5 mm in diameter (Figure 1). The Ag/AgCl reference electrode was created by electroplating. The multiplex sensor was then integrated with a microchannel made of double-coated tape as spacer and a 3D printed cap (Figure 2A-B). Performance of the sensor was evaluated in the channel by flowing different solutions and measuring the potentials of ISEs at stopped flow. The sensors were stored dry between measurements.

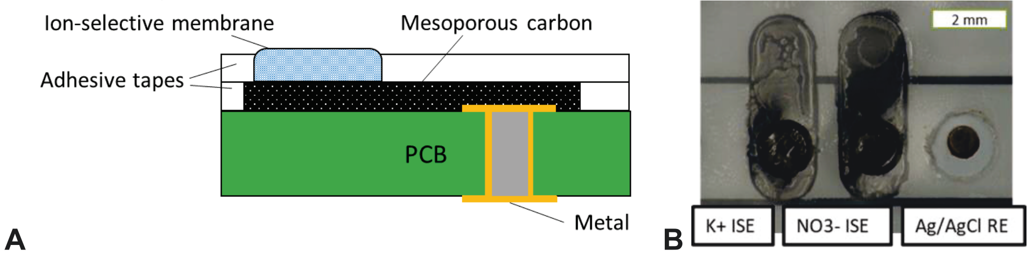

Figure 1: *A)Structure of the PCB-based multiplexed sensor. B)Photograph of the fabricated sensor.*

RESULTS AND DISCUSSION

The fabricated multiplexed sensor consisted of all-solid-state K^+ and NO_3^- ISEs, with a Ag/AgCl reference. The sensor was further embedded in a microfluidic microchannel for in-line continuous analysis (Figure 2A-B). Our preliminary results indicate that electrode response was significantly more stable when ion-selective membranes were cast away from the underlying metal pads compared to direct on top (Figure 2A-B), likely due to increased capacitance of the sensor. Both K$^+$ and NO$_3^-$ electrodes showed fast response to changing concentrations and satisfactory stability and reversibility (Figure 2C), except that in the beginning there were relatively large drifts and the conditioning time is about 10 min. These drifts can be partly associated with the Ag/AgCl reference and may be minimized by electroplating a thicker AgCl layer or employing a different reference (e.g. ionic liquid). Both K$^+$ and NO$_3^-$ electrodes displayed near-Nernstian responses of 52 mV/dec in KNO$_3$ solutions (containing 10 mM NaCl). The NO$_3^-$ electrode showed consistent sensitivities over one week, while that of the K$^+$ electrode decayed gradually (Figure 2D), most likely due to leaching of ion-exchanger (tetraphenylborate) into solutions. The baseline drift of the K$^+$ and NO$_3^-$ ISEs were 2.3 and -3.4 mV/day, respectively (Figure 2E). At such level, the sensor would require frequent calibrations, which can be automated by implementing a microfluidic control system.

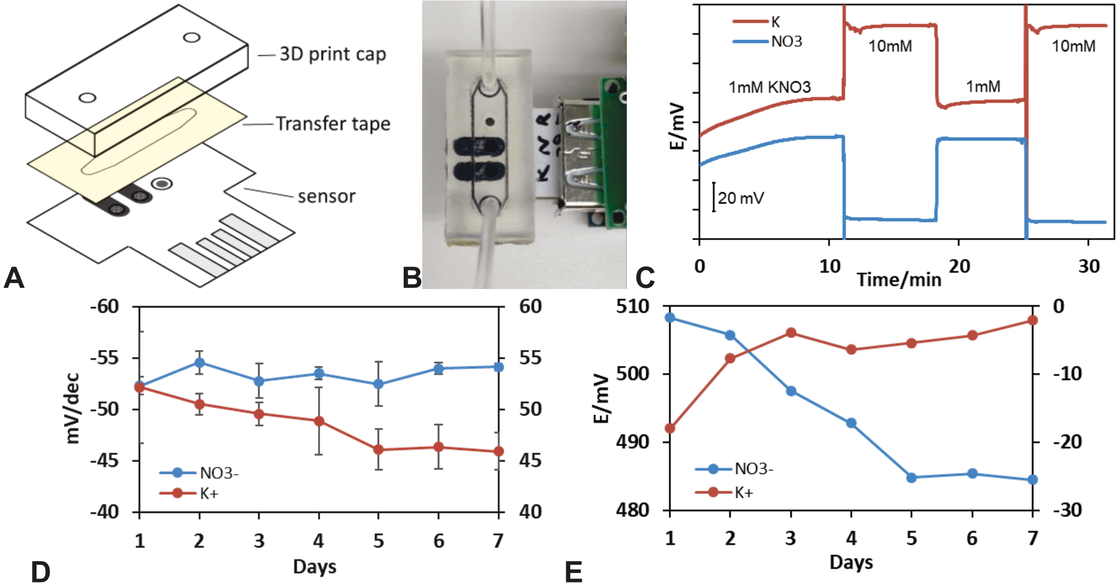

Figure2: *A)Structure of the microfluidic assembly. B)Photograph of the integrated sensor. C)Real-time response of the sensor on chip. D)Sensitivity and E)baseline drift of the sensors over 7 days. Baseline drifts were measured in 1 mM* *KNO_3.*

CONCLUSION

Multiplexed ISEs based on PCB were successfully fabricated and integrated with microfluidics. When tested in the microchannel, the sensors exhibited excellent performance in terms of sensitivity, stability and response time. Future work will focus on further improvements to stability and lifetime of the sensor, and also on evaluating its compatibility with real-world samples. These sensors can be directly interfaced with other microfluidic modules for in-line analysis of ions, or can also be integrated into portable devices for *in-situ* measurements.

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