

Engineering Spatially Patterned Selective Membranes for Scalable Multiplex Electrolyte Sensors

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Summary:

This work presents a multiplex wearable sodium-potassium sensor based on spatially patterned ion-selective membranes (ISMs) integrated onto miniaturized microelectrodes. Using masked airbrushing (AB) and doctor blading (DB) techniques, ISMs were precisely deposited onto closely spaced electrode sites, enabling scalable fabrication of compact multiplex devices. The sensors show a near-Nernstian sensitivity of 54.4 ± 0.6 mV per decade, a rapid response, good selectivity against interfering ions, and stable performance over extended operation. Linear detection ranges of 50-200 mM for sodium and 2-8 mM for potassium were achieved, with negligible pH sensitivity from pH 5.5 to 8. This platform offers strong potential for continuous electrolyte monitoring in wearable and point-of-care applications.

Keywords: wearable sensor; multiplex sensing; ion-selective membranes; sodium-potassium detection

Background, Motivation and Objective

Continuous monitoring of electrolytes is essential for maintaining physiological homeostasis and for managing disorders related to hydration, kidney function, and cardiovascular health [1]. Electrolytes such as potassium and sodium play key roles in nerve signalling, muscle contraction, fluid balance, and cardiac activity, and even small deviations from normal levels can lead to serious clinical complications [1]. For example, hyperkalemia affects more than 3.7 million people in the United States and is strongly associated with chronic kidney disease and life-threatening cardiac events [2]. In this context, wearable electrochemical sensors have emerged as promising platforms for real-time and non-invasive electrolyte monitoring in biofluids such as sweat and interstitial fluid [3].

Although wearable electrolyte sensors show considerable potential, their translation into practical devices is still limited by challenges in scalable fabrication and reliable multiplex sensing. Wearable systems must be compact, flexible, and lightweight, which requires sensing electrodes to be miniaturised to very small dimensions. However, as electrode dimensions decrease, the accurate and reproducible deposition of ISMs, which are essential for ion recognition and sensing performance, becomes increasingly difficult [4]. This challenge is further

amplified in multiplex sensor configurations, where multiple ISMs with different compositions and formulations (F1 and F2) must be patterned precisely on adjacent electrodes without overlap, cross-contamination, or loss of reproducibility.

The objective of this study is to develop multiplexed electrolyte sensors based on spatially patterned ISMs for scalable manufacturing. Specifically, this study aims to establish a fabrication strategy that enables precise and reproducible deposition of multiple ISMs onto miniaturised electrode arrays, allowing simultaneous detection of different electrolytes within a compact wearable platform. By addressing the fabrication limitations associated with multiplex ISM integration, this work seeks to support the development of scalable and high-performance wearable sensors for continuous electrolyte monitoring.

Description of the New Method or System

In this work, we developed a dual gold electroplated working electrode platform for multiplexed sodium-potassium sensing based on a conductive polymer as a transducer and spatially patterned ISMs. A common reference electrode was also designed to provide a stable potential for simultaneous multiplex measurements. ISM deposition was performed using spatial patterning strategies, including masked airbrushing (AB) and doctor blading

(DB), to achieve controlled and selective deposition of membrane formulations onto predefined electrode regions with well-defined dimensions and thicknesses. The device incorporates microfabricated electrodes with edge-to-edge spacing as low as 300 μm , together with a shared Ag/AgCl reference electrode in a compact architecture suitable for wearable applications. These patterning approaches enable precise membrane placement, minimise cross-contamination between adjacent sensing sites, and provide a promising route toward scalable fabrication of multiplex wearable electrolyte sensors.

Results

The developed sodium- and potassium-selective membranes were successfully deposited onto the microelectrode array to produce a multiplex wearable sensing platform capable of simultaneous detection of these two clinically relevant electrolytes. Spatial patterning enabled selective localisation of the sodium- and potassium-selective membranes onto closely spaced electrode sites while maintaining separation between adjacent sensing regions, demonstrating the suitability of the proposed fabrication approach for multiplex sensor integration at the microscale.

The resulting sensors with both deposition methods and different compositions exhibited near-Nernstian potentiometric performance, with an average sensitivity of 54.4 ± 0.6 mV per decade (Fig.1) [5]. The potassium sensor showed a linear response over the concentration range of 2–8 mM, while the sodium sensor operated linearly from 50–200 mM, covering concentration ranges relevant to physiological monitoring. In addition, the sensors were evaluated over a pH range of 5.5 to 8 and showed no significant pH dependence within this interval, confirming that the potentiometric response was primarily governed by the target ion activity rather than changes in sample pH.

The platform also demonstrated rapid sensor behaviour, with an immediate change in potential observed upon analyte addition, indicating fast response to concentration variations. Over extended operation, the sensors maintained stable performance for 72 h with an average drift of only 0.32 mV h^{-1} . Good selectivity was also observed against common interfering ions, including magnesium, lithium, and ammonium, confirming the ability of the ion-selective membranes to distinguish the target ions in complex electrolyte environments.

Importantly, the multiplex platform retained stable potentiometric performance for up to one week, supporting its potential for continuous

electrolyte monitoring in wearable applications. Overall, these results demonstrate that the proposed sensing platform combines miniaturised electrode architecture, precise membrane patterning, and reliable analytical performance, providing a practical pathway toward the scalable fabrication of multiplex wearable electrolyte sensors for continuous health monitoring and point-of-care diagnostics.

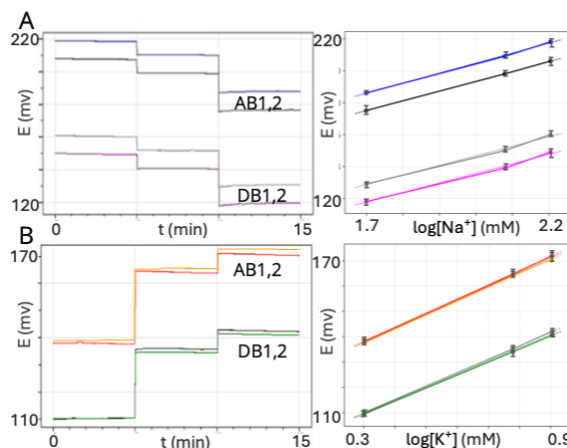


Fig. 1. Potentiometric response of the multiplex Na^+/K^+ sensor, fabricated using different deposition methods and formulations (AB1, AB2, DB1, and DB2), to mixed ion solutions with inversely varied Na^+ and K^+ concentrations. (A) The Na^+ concentration was stepped from 160 to 120 to 50 mM, while (B) the K^+ concentration was increased from 2 to 6 to 8 mM KCl, to evaluate sensor behaviour in the presence of both target ions.

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