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Self-Powered Smart Potentiometric Sensor with Relational Operation Function to Capture Concentration Excursions

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Potentiometric sensors give a spontaneous voltage response to ion concentration changes in the sample, which makes the technique promising for the realization of self-powered sensors. Previous work from our group has demonstrated that the ion-selective electrode (ISE) voltage signal may be harvested and stored by a capacitor connected in series with the electrodes. This voltage signal can be read out with a simple multimeter¹.

Based on this, our group proposed the first type of self-powered potentiometric sensor with memory.² A diode was placed in series with a capacitor in the circuit and with this design, only positive voltage changes may be recorded in the capacitor for the later readout at the end of the measurement. A Zn/Zn²⁺ electrode was used as the reference electrode (RE) to overcome the forward voltage by hundreds of millivolts. Compared to a conventional Ag/AgCl electrode, the EMF of the ion-selective electrode against the Zn RE was lifted by about 1V, sufficient to charge the capacitor with a diode placed in series. Unfortunately, however, this sensor can only record the voltage deviation in a positive direction. The voltage change in the other direction cannot be remembered because of the single direction conductivity of the diode.

In this work, we describe a self-powered sensor capable of recording both positive and negative voltage fluctuations during a period of few hours for later readout. The principle is shown in Figure 1 below and uses two different operators to capture fluctuations in the positive and negative direction. Capacitor C₁ and diode D₁ are connected to the ISE and the Zn RE for recording the positive voltage change, as established.² To record the negative voltage change, the capacitor was first charged by the ISE and the Zn RE and subsequently the switch S_{L1} was placed to position P₂ to place the diode into the circuit. The switch SL2 was then moved from position P₃ to P₄ to generate a voltage drop of about 1V across the capacitor C₂ and to overcome the forward voltage across the diode D2. Any further voltage decrease from the ISE is then recorded on the capacitor C2.

This work demonstrates a novel self-powered sensing principle that can record voltage perturbations away from a normal range over a period of hours. This sensor may be deployed as an affordable alternative option to monitor chemical changes in agriculture, aquaculture and biomedical applications.



Figure 1. Scheme of the sensor circuit. To overcome the forward voltage of the diode blocking the charge transfer, a dual reference electrode system was used here. By switching from the Zn^{2+} RE to the Ag/AgCl RE, one may generate a voltage change of about 1V, which is sufficient to discharge the capacitor in series with the diode and transfer the chemical information into the capacitor.

(1) Sailapu, S. K.; Kraikaew, P.; Sabaté, N.; Bakker, E. Self-powered potentiometric sensor transduction to a capacitive electronic component for later readout. *ACS Sens.* 2020, *5*, 2909-2914.
(2) Sailapu, S. K.; Sabate, N.; Bakker, E. Self-powered potentiometric sensors with memory. *ACS Sens.* 2021, *6*, 3650-3656.