Improving the Sensitivity of Ion-Selective Electrodes for Ultrasensitive Sensing

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Ion-selective electrodes (ISEs) remain the gold standard for the determination of ions in complex samples ranging from clinical samples to environmental waters. They are operated at zero current and their phase boundary potential relates to the sample activity (Figure 1A). Their sensitivity follows the Nernst equation and is ideally 59.2 mV/log*a* at 25 °C for a singly charged positive ion. Unfortunately, this limited sensitivity poses challenges to measure small activity fluctuations that are critical in applications like seawater pH monitoring and blood sodium measurements.

Our group previously reported increased sensitivity with membrane-based ISEs (Figure 1B) [1]. A capacitor is placed in series with the ISE and the cell potential is kept constant. Thus, any potential change at the ISE induces a transient current on the capacitor. The charge is then used as analytical signal. As the transient current needs to flow through the ISE, this method is not compatible with highly resistive ISEs such as pH glass electrodes.

Our latest work puts forward a novel approach that combines zero current measurement at the ISE and coulometric readout by implementing a high impedance voltage follower in the circuit (Figure 1C) [2]. This enables the use of any ISE with the coulometric protocol. The setup is evaluated with a glass electrode in narrow pH ranges comparable to that for environmental samples with 0.01 pH steps, achieving 64 µpH precision, and over a wider pH range (4 to 10) to demonstrate the versatility of this approach.

Ongoing improvements include the development of a submersible probe for ultrasensitive *in situ* pH measurements in natural waters and the investigation of a flow system for multi-ion detection in clinical samples.

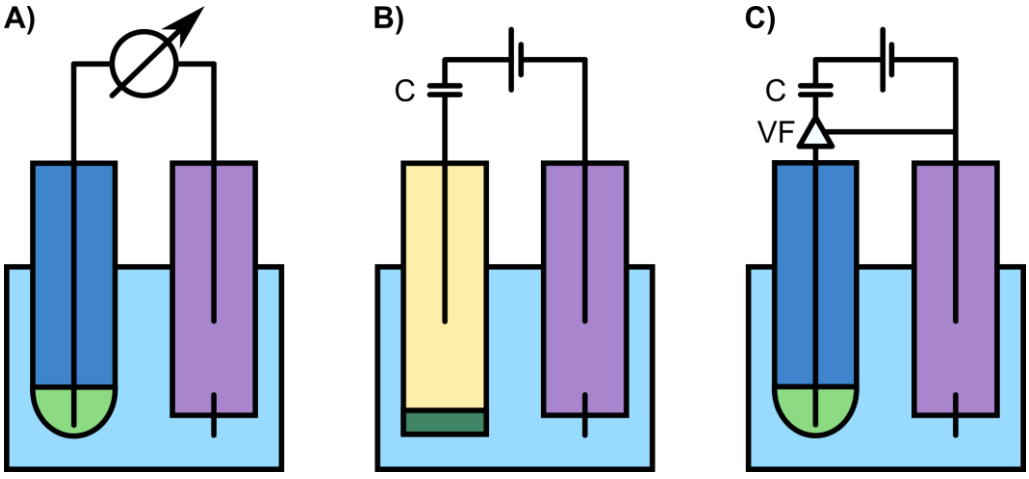

Figure 1. A) Zero current potentiometry with pH glass electrode. B) Coulometric readout with membrane-based electrode. C) Novel coulometric setup with a high impedance voltage follower.

[1] P. Kraikaew, S. Jeanneret, Y. Soda, T. Cherubini, E. Bakker, ACS Sens., 2020, 5 (3), 650-654.
[2] R. Nussbaum, S. Jeanneret, E. Bakker, Anal. Chem. 2024, 96 (16), 6436-6443.