Coulometric Readout of pH Glass Electrodes for Increased Sensitivity

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Glass electrodes are considered the gold standard for routine pH determination. They are operated at zero current and the phase boundary potential at the glass-sample interphase relates to the solution pH (Figure 1, A). Their sensitivity is dictated by the Nernst equation and is ideally -59.2 mV/pH at 25°C. However, this limited sensitivity poses challenges for measuring small pH fluctuations that are critical in applications like seawater pH monitoring.

Our group previously reported on increasing sensitivity with pH membrane-based electrodes (Figure 1, B). For this approach, an electronic capacitor is placed in series with the pH electrode and the cell potential is kept constant. Therefore, any potential change at the sensing electrode induces an opposite change on the capacitor that charges with a transient current. The charge is obtained from the latter and is used as analytical signal. However, the transient current must flow through the electrochemical cell, which may induce measurement errors and makes it impossible to use glass electrodes because of their high impedance.

Our most recent work proposes a novel approach that combines zero current measurement at the pH electrode and a high impedance input voltage follower (Figure 1, C). This allows the use of a glass electrode with the coulometric protocol. The setup is evaluated with narrow pH ranges comparable to that for environmental samples with 0.01 pH steps, achieving 64 µpH precision, and to a wider pH range (4 to 10) to assess the versatility of the setup. Further improvements are underway to adapt this method for a submersible probe, allowing for ultrasensitive *in situ* pH measurements.

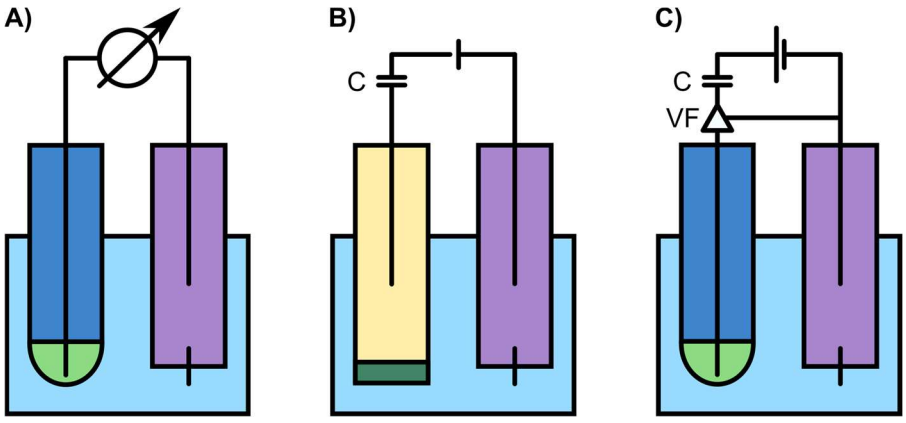

Figure 1. A) Potentiometry with glass electrode. B) Coulometry with membrane electrode. C) Coulometry with voltage follower and glass electrode.

References:

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[2] R. Nussbaum, S. Jeanneret, E. Bakker, *Anal. Chem.* **2024**, 96 (16), 6436-6443.