Improving the Sensitivity of pH Glass Electrodes with an Alternative Readout

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Glass electrodes are the gold standard for day-to-day pH determination. They are typically operated at zero current and the phase boundary potential at the electrode-sample interface relates to the sample pH. The sensitivity of such electrodes is dictated by the Nernst equation and is equal to -59.2 mV/pH at 25°C. This limited value makes very small pH variations challenging to measure. Yet, their accurate monitoring is crucial to keep track of environmental processes such as ocean acidification (-0.002 pH y^{-1}) or metal speciation [1].

Constant potential coulometry was introduced to improve the sensitivity of ion-selective electrodes (ISEs) compared to the Nernstian response [2]. In this protocol, a constant potential is imposed between the reference electrode (RE) and the ISE. Thus, any potential change at the ISE-sample interface induces an opposite potential change on an electronic capacitor placed in series, resulting in a transient current. The charge is obtained from the latter and used as amplified analytical signal. Unfortunately, the transient current must flow through the electrochemical cell, which may induce measurement errors and makes it impossible to use high impedance ISEs such as glass electrodes.

We report here on an electronic circuit that overcomes these limitations through the combination of (i) zero-current measurement at the ISE and (ii) a high-impedance input voltage follower [3]. As the transient current does not flow though the ISE, its potential is left intact and a counter electrode is no longer required. The setup is first evaluated for chloride sensing as model system and compared with classical potentiometry. The procedure is then successfully applied with a glass electrode (i) to narrow pH ranges comparable to the values found in environmental samples with 0.01 pH steps (64 µpH precision) and (ii) to a wider pH range (4 to 10) with 1 pH steps to assess the versatility of the proposed method.
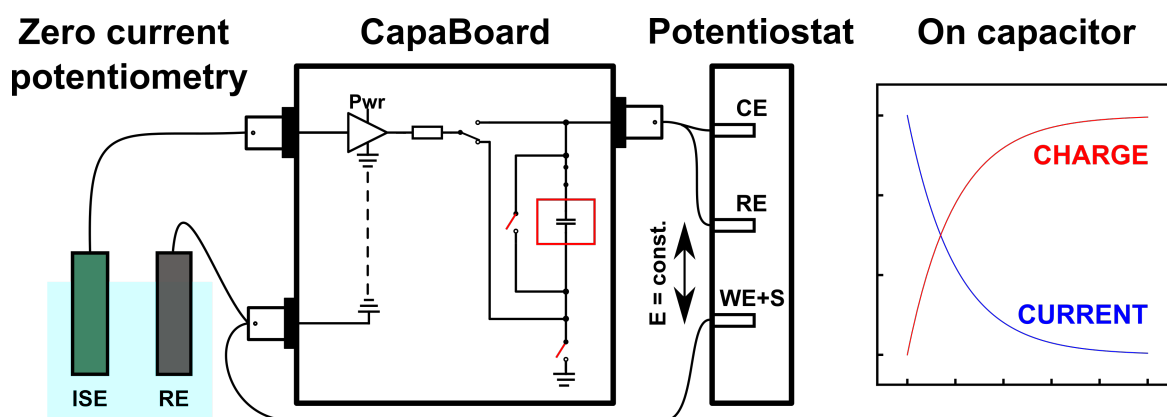

Figure 1. Scheme of the novel experimental setup for enhanced pH sensitivity.

[1] R. N. Bates, M. H. P. Best, K. Neely, R. Garley, A. G. Dickson, R. J. Johnson, *Biogeosciences*, **2012**, 9(7), 2509-2522.
[2] T. Han, U. Mattinen, J. Bobacka, *ACS Sens.*, **2019**, 4(4), 900-906.
[3] R. Nussbaum, S. Jeanneret, E. Bakker, *Anal. Chem,* in revisions.