

Microfabricated Self-Referencing Pulstrodes

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With an ever-increasing world population and life expectancy, public health often ranks as the second sector in terms of budgetary spending worldwide. Finding ways to reduce the costs, whether it is in the preventive care or therapeutic domain, is a crucial component of developing a sustainable health system. As a result, Point-of-Care Testings (POCTs) and wearable sensors have attracted a tremendous interest in the past decades. As opposed to traditional analysis, which are costly and time-consuming, POCTs and wearable sensors present, among others, the following advantages: they are cost-effective and allow rapid or continuous measurements, which lead to better reaction time and thus fewer costly complications [1]. Electrochemical sensors in that regards represent a good example of POCTs.

The reference electrode is an essential component of an electrochemical system, resulting in a high research activity in that domain [2]. The gold standard remains the Ag/AgCl double junction reference electrode. However, owing to its electrolyte-filled inner compartment its design is cumbersome and impractical for wearable sensors applications, which require miniaturization. From that point of view, all-solid state reference electrodes provide a promising alternative.

Gao *et al.* proposed a solid-state reference electrode which relies on an Ag/AgI element and acts as a pulstrode to self-generate a reference potential [3]. The pulstrode protocol consists of four distinct steps: 1) potentiometric measurement of the initial state of the system (OCP), 2) a cathodic current pulse, leading to the reduction of Ag⁺ into Ag and the local release of a controlled amount of iodide, 3) measurement of the EMF (reference pulse) 4) application of the original OCP to regenerate the system into its initial state. The protocol has proven its reliability in terms of precision and stability over cycles on a macro-electrode.

In the present context of finding a reference electrode suitable for miniaturized systems, this work investigates the use of the pulstrode protocol on inkjet-printed electrodes in collaboration with the Swiss Center for Electronics and Microtechnology (CSEM). The performance of the inkjet-printed electrodes as reference element are compared to a classical reference element (double-junction silver chloride reference electrode) for the quantification of major ions in biological matrixes.

Additionally, an attempt to improve the robustness of the described system against sample convection and sample density fluctuations was made by covering the electrode surface with an agarose gel layer.

[1] A. Lewenstam, *Electroanalysis*, **2014**, 26 (6), 1171–81.

[2] H. Jinbo, A. Stein and P. Bühlmann, *TrAC Trends in Analytical Chemistry*, **2016**, 76, 102–14.

[3] W.Gao, E. Zdrachek, X. Xie, and E. Bakker, *Angewandte Chemie International Edition* 59, **2020**, 59 (6), 2294–98.