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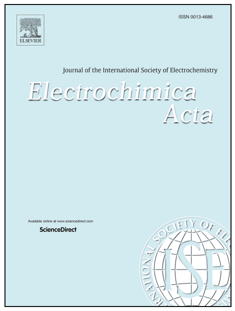

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Long-Term Stability of Screen-Printed Pseudo-Reference Electrodes for Electrochemical Biosensors

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ABSTRACT: Pseudo reference electrodes forms an essential part of electrochemical transducers, where they are used to maintain a reference potential for the system. Yet, little is known about their long-term stability, and any drift may cause undesired changes in the sensor signal. This paper investigates the stability of the reference potential of five material systems of screen-printed reference electrodes. Their potential was continuously monitored for a duration of 40 days in a phosphate buffered solution, and any signal changes were corroborated with EDX elemental analyses, SEM micrographs and cyclic voltammetry. The electrodes were considered to be stable as long as they remained within 30 mV of their initial potential throughout the study. It was found that Ag/AgCl electrodes with a 3:1 atomic ratio kept a stable reference potential (±2.2 mV), whereas Ag/AgCl electrodes with a 9:1 atomic ratio, despite showing good overall constancy of ±3.2 mV, seemed to statistically lose stability towards the end of the 40 day trial due to AgCl depletion through dissolution. The daily potential drift for the respective Ag/AgCl electrodes were −0.2 mV (3:1 ratio) and −0.1 mV (9:1 ratio), suggesting a proportionality between the amount of dissociated AgCl close to the electrode surface and the initial AgCl loading. Electrodes consisting of only Ag showed tendencies towards a mixed potential contribution, which reduced the long-term stability (±24.2 mV) as well as the longevity span (2 days). Ag/Pd electrodes proved to be more unstable (±29.7 mV), with an average lifetime of around 3.5 days. Pt had the greatest potential instability (±59.8 mV), rendering its average lifetime to less than a day. It was shown that electrodes which deviates from the Ag/AgCl equilibrium had the greatest potential variation with time.

1. Introduction

The reference electrode provides a stable and known potential towards which the working electrode of an electrochemical cell can be controlled or measured.[1] This is important in potentiometric sensors, where any offset or drift in the reference electrode potential would lead to a direct change in the output signal. For potential-controlled sensors this could result in (i) a change in the electron transfer rate of the targeted reaction, (ii) undesired side reactions of electrolyte constituents, and even of the electrode material itself, or (iii) remain unaffected due to other rate determining processes.[1,2] It is therefore important that the reference electrode potential remains within a limit which mirrors the predefined accuracy of the biosensor throughout its operational lifetime.

Screen-printing is a popular way of making reference electrodes (SPREs). These electrodes have historically been used in one-shot type measurements in disposable low cost consumer diagnostics or therapeutics.[3] Growing interest in uninterrupted gathering of sensor data over longer periods of time sets higher requirements to the stability of the measurement cell. This is especially important for sensors operating in remote or inaccessible locations, where replacement is difficult and costly.[4,5] The properties of electrodes used in electrochemical cells are sensitive to changes in structure and composition on both sides of the electrode-electrolyte-interface. It is evident that a sensor system which is exposed to the environment for a longer period will have an increased probability of succumbing to structural and