All Covalently Bound Ion-Selective Membranes for Increased Stability in Potentiometric Sensing

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Solid-contact ion-selective electrodes have gained significant interest over the last decade due to their ease-of-use, miniaturisation possibilities and low maintenance. They can now be routinely found in the bioanalytical field where they are used to measure a range of blood electrolytes or in environmental monitoring where they enable the continuous measurement of a wide range of relevant ions, such as nitrate, pH or carbonate. Solid contact ion-selective electrodes include an electron conducting material, such as glassy carbon or gold, covered by a transducing material that is known to improve the stability of the signal and suppress undesired ion transport. The last component is a poly(vinyl chloride) (PVC)-based plasticised membrane loaded with ion-exchanger and ionophore that enable selective and sensitive sensing of the target analyte. Unfortunately, this system may suffer from leaching of membrane components that over time causes drift and loss of sensitivity[1], especially when their thickness is reduced to the nanoscale.

We present here a new strategy for creating leak-free ion-selective plasticised membranes. Drawing inspiration from previous work on single membrane component covalent attachment based on a plasticiser-free cross-linked poly(decyl methacrylate matrix)[2-3], we decided here to take advantage of “click” chemistry, also known as azide alkyne cycloaddition, to safely anchor membrane components. Chlorine groups naturally present on PVC can be replaced by azide groups, thus generating an appropriate platform to perform “click” reactions. A similar strategy was already previously developed in our group where “click” chemistry was used to attach a ferrocene molecule to PVC in order to create a transducer-free ion-selective electrode[4]. In our case, the aim is to modify membrane components, and the transducing element in a second step, to include an alkyne group, needed for the final covalent attachment. Taking advantage of the high yield of “click” reactions, alkyne-modified membrane components can then be covalently attached in a quantitative manner by controlling the stoichiometry to achieve a leak-free ion-selective membrane. These new electrodes will be tested using thin-layer membranes[5] to accelerate the leaching process and confirm their improved performances compared to conventional membranes that only rely on lipophilicity.

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