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 wide range of blood electrolytes or in environmental monitoring where they enable the continuous measurement of a large 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 polyvinyl chloride (PVC)-based plasticised membrane loaded with ion-exchanger and ionophore that enable the selective and sensitive sensing of the target analyte. Unfortunately, this system suffers from leaching of membrane components that over time causes drift and loss of sensitivity[1]. To minimise components leaching, different strategies were envisioned such as enhancement of lipophilicity[2] or covalent binding[3]. Increasing the lipophilicity only slows down the leaching and can also be detrimental in terms of synthetic modification and solubility in organic media. The second approach was based on a plasticiser-free cross-linked poly(decyl methacrylate) matrix that was functional if a single membrane component (either ion-exchanger or ionophore) was covalently attached. Although some studies on the topic exist, reports of attempting the covalent linking of all membrane components[4-5] are scarce.

We present here a new strategy for creating a leak-free ion-selective plasticised membrane, where we decided here to take advantage of “Click” chemistry to safely anchor membrane components. Chlorine groups naturally present on PVC can be easily replaced by azide groups, thus generating an ideal platform to perform a “Click” reaction, also known as azide alkyne cycloaddition. Membrane components can in a second step be modified 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 be covalently attached in a quantitative manner by controlling the stoichiometry to prevent any leaching. The new electrodes will be tested using thin-layer membranes[6] to accelerate the leaching process and confirm their improved performances compared to conventional membrane that only rely on lipophilicity.

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