

Recognizing Ionic Species with New Sensing Concepts

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Abstract

This talk will report on recent conceptual advances in the field of membrane electrodes and ion optodes, including color readout for membrane electrode and ion optodes that work independently of solution pH. It will describe how charge readout of membrane electrodes can be realized as an alternative to potentiometry. And it will show how an illuminated spot on poorly doped silicon can turn on dynamic electrochemistry at that chosen location, and how this may be used to develop light addressable ion sensors.

Key words: membrane electrodes, ionophores, optodes, bipolar electrodes, light addressable sensors.

Optical Ion Sensors

The realization of a fundamentally sound optical transduction of membrane electrodes has been a goal for many years. It all started by observing chromogenic ionophores that changed their optical properties upon binding with a host molecules in a membrane film thinner than the ones used in potentiometric probes. In a sweeping paper by Morf where he aimed to impress the audience of the Matrafured conference, he put forward the principles by which so called bulk optodes must function, namely on the basis of ion-exchange and coextraction equilibria between the aqueous and sensing phase. Unfortunately, this meant that one could not realize an optical readout for single ions, which is really what one would like to achieve. Some progress in this direction has been recently achieved by the use of solvatochromic dyes that function not only as the exchanging reference ion but also as the transducing molecule as their optical properties change upon transfer into the aqueous phase. The lipophilization of these probes made it possible to confine this exchange just the sensor surface, realizing self-contained optical ion probes [1].

Color Readout for Potentiometric Probes

The concept described here directly translates membrane electrode response to an optical

readout by bipolar electrodes [2]. This is a principle that overcomes the limitations described above and results in optical sensors that are no more fundamentally compromised than potentiometric sensing probes.

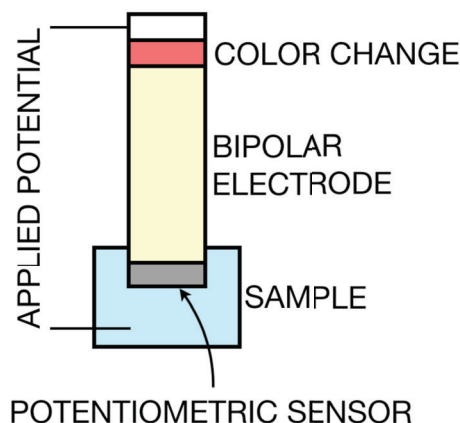


Fig. 1. Schematic of a colorimetric potentiometric probe using bipolar electrochemistry principles.

It is realized by an imposed potential across a free hanging (bipolar) electrode that makes contact on one end with the sample (the sensing probe) and on the other with a reference solution optimized for optical readout, see Fig. 1. As the sample concentration changes, the potential at the sample side is altered predictably according to the Nernst

equation, and this change must be compensated at the opposite end of the bipolar electrode and translated into an optically detectable change. A number of examples will be shown to illustrate the principle, one with a colorimetric dye on the detection side and either Ag/AgCl or a polymeric ion-selective membrane on the sample side, the other using fluorescent dye transducers. The principle may be multiplexed for large arrays of electrodes to achieve chemical imaging applications where the sample does not need to be exposed to light.

Charge Readout of Membrane Electrodes

Bipolar ion-selective electrodes may also be read out coulometrically, forming an alternate methodology that compares favorably to potentiometry (Fig. 2). The concept has been put forward by Bobacka's group [3] and further developed by us. Here, a constant potential is applied across the electrode, resulting in a potential change at a buried capacitive transduction layer that must be exactly opposite the potential change at the sample–membrane interface. This results in a highly sensitive charge readout for ion-selective electrodes that allows one to assess extremely small concentration changes in the sample.

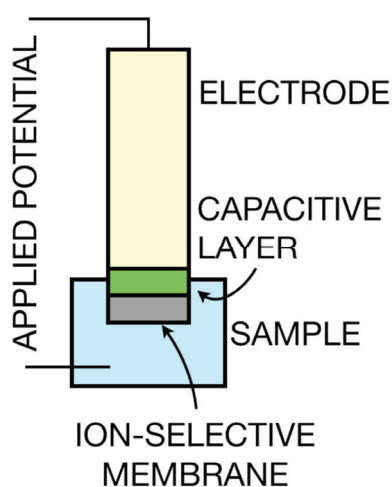


Fig. 2. Schematic of a coulometric ion sensing probe using a capacitive intermediate layer. The probe is held at a constant potential.

Light Addressable Ion Sensors

Another combined technique will be presented with light addressable membrane electrodes. A poorly doped silicon electrode can be made conductive by shining light on a defined spot, and electrochemistry will turn on at that illuminated spot only [4]. Such silicon electrodes have been modified ferrocene monolayers and subsequently spin cast with a thin polymeric sensing film to render them ion selective.

Such films are interrogated by cyclic voltammetry and the resulting surface confined peak shaped ferrocene current response is found to shift with changing ion concentration in the sample. As an early application the release of potassium from cells adhered onto the modified electrode is successfully observed.

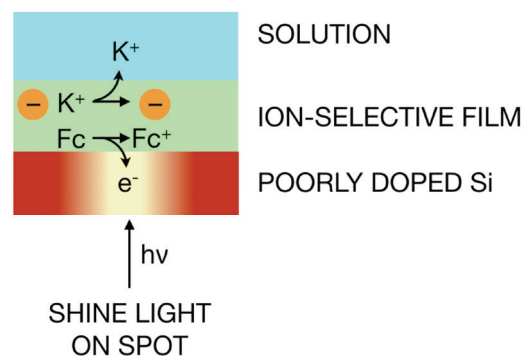


Fig. 3. Schematic of a light addressable electrode modified with an ion-selective membrane coating.

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