

Voltammetric Thin Layer Ion Selective Membranes

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Abstract

Voltammetric thin layer ion selective membranes (ISMs) that consist of two layers, an outside thin polymeric sensing layer and an inner conducting polymer layer, are introduced here. This voltammetric ISM can be used for sensing application within two modes: a stripping mode and a potentiometric mode. Transitions between the two modes and concentration limit for each mode are both experimentally explored and theoretically modelled by finite difference method. Simulation agrees well with experimental data. Besides its sensing application, this voltammetric thin layer ISM can also be applied for probing ion-ionophore interactions inside the membrane. Valinomycin is firstly put forward here as a model ionophore, for which formal complex formation constants with potassium and sodium are easily determined. Other molecular receptors that exhibit reversible binding kinetics are also investigated.

Key words: Ion selective membranes, voltammetry, simulation, ionophore, thin layer

In contrast to the traditional liquid ion selective membrane with thickness of hundreds of micrometers, thin layer polymeric ion selective membranes (ISMs) only have membrane thickness on the order of several micrometers to several hundred nanometers.^[1] Instead of using silver/silver chloride wire and inner reference solution as transducing element, the thin layer ISMs are fabricated by spin coating a few pre-prepared membrane cocktails on an inner transducing layer, usually using conducting polymers. The conducting polymers, such as poly(3-octylthiophene) (POT)^[3] and poly(3,4-thylenedioxythiophene) (PEDOT)^[4] that are previously electropolymerized on a glassy carbon or gold electrode, exhibit a stable electrochemical behavior and possess enough electron capacity. Electrically excited oxidation or reduction of this inner transducer will trigger an extraction or repulsion of ion exchangers from/into the outside thin layer ISM. Simultaneously, the counter ion of the ion exchanger should be expelled into or extracted from the sample solution, due to an electroneutrality condition of the whole membrane. It is this concomitant repulsion/extraction process by conducting polymer oxidation/reduction that generates voltammetric signals of the thin layer ISMs.

The thin layer ISMs were firstly applied for sensing of ions. For instance, solid state thin layer ISMs with POT or PEDOT as inner transducers were successfully used for stripping voltammetric detection of nanomolar heparin,^[5] perchlorate,^[1] ammonium, potassium^[4] and even subnanomolar calcium.^[6] The utilization of this technique was divided into two steps. First, a constant potential was applied for a certain long time for continuously pre-accumulating the sample ion from solution to ISM. Then, a reverse fast linear potential scan was applied, repelling the ion again to aqueous solution, resulting in a stripping current that is linear against the sample concentration. Recently, our group found that at relatively high sample concentration, thin layer ISM is fully saturated by sample ions and once it is, the voltammetric peak potential shifts to more positive positions, following a Nernstian displacement with increasing sample concentrations.^[2] Regarding with this nature, we developed a multi-ions potentiometric sensor by incorporating several ion selective carriers in one ISM, obtaining multi-ions calibration curves within only one electrode, thereby opening a new sensing mode of this ISM. According to this strategy, lithium and potassium in human plasma were determined.^[3]

In order to better utilize the two sensing modes, it is very important to know the concentration limit of each mode and identify the transitions between them. In this presentation, a selective silver ISM is chosen as a model system that experimentally shows two distinct concentration ranges. At low silver concentration, voltammetric peak current is influenced by stirring and rotating, proving that the voltammetry signal is diffusion controlled. It is this diffusion control that forms the basis for stripping voltammetry. At high silver concentration, no stirring effects are observed and peak current is linear with scan rate, showing no diffusion dependency. The simulation of the system corroborates the existence of two concentration ranges and proves that diffusion could be neglected at high sample concentration. Detection limits are also predicted by modeling.^[7, 8]

In addition to interrogating sample compositions, thin layer ISM could also be used for probing ion-ionophores interactions. The barrier for this purpose is how to get a correct potential distribution between ion transfer potential and potential for inner polymer reduction/oxidation. The problem is here overcome by recording the behavior of the membrane towards a bulky reference ion, tetrabutylammonium. This cation exhibits a voltammetric phase transfer that is well described theoretically and confirmed experimentally to be independent of ionophore. This information is used to arrive at a relationship between charge and potential for the transducing layer alone, which is then subtracted in subsequent experiments from the experimental cell potential. This allows one to describe, in a single linear scan, the change in phase boundary potential as a function of ion-exchanger concentration. Fitting of this function now gives direct information on complex stoichiometry, complex formation constants, and selectivity coefficient as a function of ion-exchanger. The principle is put forward with valinomycin as a model ionophore. Other ionophores that exhibit reversible binding kinetics are also investigated.

References

- [1] Y. Kim, S. Amemiya, *Anal. Chem.* 80, 6056-6065. (2008); doi: 10.1021/ac8008687
- [2] G. A. Crespo, M. Cuartero, E. Bakker, *Anal. Chem.* 87, 7729-7737. (2015); doi: 10.1021/acs.analchem.5b01459

- [3] M. Cuartero, G. A. Crespo, E. Bakker, *Anal. Chem.* 88, 5649-5654. (2016); doi: 10.1021/acs.analchem.6b01085
- [4] B. Kabagambe, A. Izadyar, S. Amemiya, *Anal. Chem.* 84, 7979-7986. (2012); doi: 10.1021/ac301773w
- [5] J. Guo, S. Amemiya, *Anal. Chem.* 78, 6893-6902. (2006); doi: 10.1021/ac061003i
- [6] B. Kabagambe, M. B. Garada, R. Ishimatsu, S. Amemiya, *Anal. Chem.* 86, 7939-7946. (2014); doi: 10.1021/ac501951m
- [7] D. Yuan, M. Cuartero, G. A. Crespo, E. Bakker, *Anal. Chem.* 89, 586-594. (2017); doi: 10.1021/acs.analchem.6b03354
- [8] D. Yuan, M. Cuartero, G. A. Crespo, E. Bakker, *Anal. Chem.* 89, 586-594. (2017); doi: 10.1021/acs.analchem.6b03354