IONIC RECOGNITION AND SELECTIVE RESPONSE IN SELF ASSEMBLING MONOLAYER MEMBRANES ON ELECTRODES

FIELD OF THE INVENTION:

There are provided selective electrodes for use in electrochemical sensing devices. There is provided a method for the production of such electrodes. The novel selective electrodes are characterized by a surface layer, generally an organic monolayer comprising an inert monolayer matrix in which there are embedded synthetic "receptor sites" adapted to provide species selectivity. The inert matrix blocks vacant sites on the surface and thus prevents the approach of undesired species to the surface of the electrode. The electrode is made of an electrically conducting substance, to which the monolayers including the inert and active species of the monolayer is bonded.

BACKGROUND OF THE INVENTION:

Impermeable one-molecule thick barriers for ions and water have been produced on gold, using techniques of monlayer self-assembly (Sabatani et al., J. Phys. Chem. 91 6663-9 (1987)).

To confer ion-specificity to a metal electrode, the mere binding of ion-specific molecules to the electrode surface is not enough, as there must be prevented leakage of other, undesired species which might react electrochemically at the electrode.

SUMMARY OF THE INVENTION:

There is provided an electrode, made of a non-specific electrically conductive material, coated with a stable ion-selective monolayer which, in certain aspects, is similar in performance to basic structural and functional principles of natural bilayer membranes. The process of the invention is based on the self-assembly of such monolayer structures. The essentially monolayer surface coatings applied to non specific conductive substrates comprise an inert molecular matrix in which there is embedded a second component, providing specific synthetic receptor sites. In particular cases it is possible to produce the surface layer from a substance which fulfills both such functions. The monolayer-coated electrodes of the invention are capable of recognizing selected species out of a mixture of a variety of species. They are especially suited to recognize certain ionic species in a system containing such species in a mixture with other, otherwise interfering species. The inert matrix prevents interference of such undesired species by preventing their access to the immediate vicinity of the electrode surface.

The invention also relates, as pointed out above, to a process for the production of such selective monolayers and electrodes coated therewith. The invention also relates to the use of such electrodes in electrochemical sensing devices and to assays based on the use of such electrodes. The invention relates to the deposition of organic films of molecular thickness (monolayers) on a suitable electrically conducting solid surface to be used as electrode in an electrochemical process, which organic film functions as a selective ultrathin membrane conferring chemical selectivity (specific responses) to the electrode in a selected electrochemical process.

The chemical selectivity of the monolayer membranes of the present invention is a consequence of their double function as:

a) Dense molecular barriers efficiently blocking passage to the electrode of undesired chemical species from a fluid phase contacting the electrode;

b) Specific receptors for certain chemical species in the fluid phase, for which electrochemical detection at the electrode is required.

Monolayer membranes providing such double function capability are, in general, made of one or more molecular components, at least one of which (the "specific receptor" component) displays binding and/or permeation specificity towards one or more selected species in the fluid phase, and, at least one of which (the "blocking" component) prevents undesired species from the fluid phase from approaching the electrode surface to a distance at which their electrochemical detection by the electrodes will occur. It is also possible to use only one component which provides both membrane functions, i.e. that of the specific receptor for certain selected species, and that of an efficient blocking barrier for other, undesired species.

As specific receptor components there can be used any molecule which can be incorporated in a solid-supported monolayer and which is capable of allowing the passage of certain selected chemical species to the electrode, or which can immobilize certain such species at a distance from the electrode surface that is sufficiently small to permit measurable exchange of electrical charge with the electrode and thus detection of electrochemical activity. Suitable receptor components may be, for example, molecules which, when incorporated in a stable monolayer on the electrode surface, can bind selected ions or molecules from solution through complex formation, or are provided with well defined molecular-size channels through which such selected species from solution may diffuse to the electrode. Blocking components are molecules which can be part of a solid-supported monolayer and which fill free spaces (pinholes) in the monolayer membrane, including molecular-size pinholes, while providing a sufficiently thick and compact layer through which species from the fluid phase that are not "recognized" by the receptor component cannot diffuse to the electrode surface or approach it to a distance at which measurable exchange of electrical charge with the electrode will be detected. The fluid phase may be any liquid, gas, solution in a liquid or in a gas, or any viscous liquid, solid material, or solution in such materials, which can contain mobile chemical species that are electrochemically active and may thus participate in, or affect electrochemical processes. As chemical species in the fluid phase one may consider any molecule or ion, organic, inorganic, or of biological origin, which may undergo or affect any electrochemical process at an electrode surface, and, thus, may be detected electrochemically through such process. For the deposition of monolayer membranes on solid electrode surfaces, of the type pertinent to the present invention, one can use processes such as adsorption, chemisorption, or electrochemical deposition of the membrane components from any suitable organic or aqueous solution, from a gaseous phase, or from the melt of the membrane components. The membrane components may be deposited on the electrode surface simultaneously or sequentially. A compound fulfilling both functions can be used.