

8.3.3 Chemically modified electrodes

Chemically modified electrodes (CMEs) comprise an approach to electrode system design that find use in

1. a wide spectrum of basic electrochemical investigations, including the relationship of heterogeneous electron transfer and chemical reactivity of electrode surface chemistry, electrostatic phenomena at electrode surface, and electron as well as ionic transport phenomena in polymers, and
2. the design of electrochemical devices and systems for applications in chemical sensing, energy conversion and storage, molecular electronics, electrochromic displays and electro-organic synthesis.

Compared with other electrode concepts in electrochemistry, the distinguishing feature of a CME is that a quite thin film (from monomolecular to perhaps a few micrometers in thickness) of a selected substance is bonded to or coated on the electrode surface to endow the electrode with the chemical, electrochemical, optical, electrical, transport, and other desirable properties of the film in a rational chemically designed manner. The range of electrode surface properties sought is broader than that of ion-selective electrodes (ISEs) which also involve, in their highest forms, rational design of the phase-boundary, partition and transport properties of membranes on or between electrodes. CMEs also differ from ISEs in that they generally are used amperometrically, a faradaic (charge transfer) reaction being the basis of experimental measurement or study, whereas ISEs are generally used in potentiometric mode where a phase-boundary potential (interfacial potential difference) is the measured quantity. Gas-sensing electrodes (e.g., for CO₂, NH₃, NO_x) are also potentiometric electrodes, although the Clark oxygen electrode, which operates amperometrically, is an exception. Chemically sensitive field effect transistors (ChemFETs) are basically non-faradaic electrode systems in which electric field variations in the semiconductor gate region control the magnitude of the source-drain current. Enzyme electrodes detect the product(s) of a reaction between an immobilized enzyme layer and a reaction substrate in many ways, including both amperometric and potentiometric means. The distinction between CMEs and amperometric enzyme electrodes is thus very narrow, the latter being based on a natural biological catalyst, but also with a rational (bio)molecular electrode design goal in mind.

Terms and definitions

Chemically modified electrode (CME)

An electrode made of a conducting or a semiconducting material that is coated with a selected monomolecular, multimolecular, ionic, or polymeric chemical film and by means of faradaic (charge-consuming) reactions exhibits chemical, electrochemical, and/or optical properties of the chemical film.

Electron transport through the film

Processes by which electrochemical charge is transported through films of chemicals to a conducting or semiconducting underlying material by electron self-exchange, electron self-exchange coupled to physical diffusion, and conduction by highly conjugated molecular components of the film.

Coverage (in Modified Electrodes)

The area-normalized quantity of a designated kind of a chemical site in the chemical film. Coverage must be distinguished as to total mol/m² present versus mol/m² that are electrochemically reactive or accessible on some given timescale.

Biosensor

A special type of CME or ISE based on a biochemical recognition process; the biosensor surface is modified by the attachment of a biocomponent (e.g., enzyme, antigen/antibody, certain Langmuir-Blodgett films, liposomes, plant or animal tissue, etc.) which functions as the chemoreceptor. (Alternative term: *bioanalytical sensor*).

Chemoreceptor

A selective receiving site for analyte recognition and reaction. In the case of a biologically derived receptor, the more specific term *bioreceptor* may be used.