CHEMICALLY MODIFIED ELECTRODES: 
RECOMMENDED TERMINOLOGY 
AND DEFINITIONS

(IUPAC Recommendations 1997)

Prepared for publication by

R. A. DURST1, A. J. BÄUMNER2, R. W. MURRAY3, R. P. BUCK3, AND C. P. ANDRIEUX4

1Analytical Chemistry Laboratories, Cornell University, Geneva, NY 14456, USA
2Institute for Technical Biochemistry, University of Stuttgart, D-70569 Stuttgart, F.R. Germany
3Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514, USA
4Laboratoire d'Électrochimie Moléculaire, Université de Paris 7, 75251 Paris Cedex 05, France

*Membership of the Commissions during 1985–91 when the Report was prepared was as follows:

Commission on Environmental Analytical Chemistry (LLTC)


Commission on Electroanalytical Chemistry

Chairman: K. Izutsu (Japan; 1985–87); M. Senda (Japan; 1987–89); R. Durst (USA; 1989–91); Vice-Chairman: E. Pungor (Hungary; 1985–87); R. Kalvoda (Czechoslovakia; 1987–89); M. Senda (Japan; 1989–91); Secretary: M. Senda (Japan; 1985–87); R. Durst (USA; 1987–89); K. Kadish (USA; 1989–91); Titular Members: J. Buffle (Switzerland; 1985–89); J. Juillard (France; 1985–87); M. Gross (France; 1987–91); K. Kadish (USA; 1985–89); R. Kalvoda (Czechoslovakia; 1985–87); K. Stulik (Czechoslovakia; 1989–91); K. Töth (Hungary; 1987–91); R. Buck (1989–91); Associate Members: R. Buck (USA; 1987–89); K. Cammann (FRG; 1989–91); M. F. Camoes (Portugal; 1987–91); A. Covington (UK; 1985–87); W. Davison (UK; 1985–89); R. Durst (USA; 1985–87); A. Fogg (UK; 1987–91); M. Gross (France; 1985–87); H. Kao (China; 1985–89); M. L'Her (France; 1985–91); R. Kapoor (India; 1985–89); H. van Leeuwen (Netherlands); Y. Marcus (Israel; 1985–87); T. Mussini (Italy; 1985–87); J. Osteryoung (USA; 1985–89); S. Rondinini Cavallari (Italy; 1985–87); K. Stulik (Czechoslovakia; 1987–89); N. Tanaka (Japan; 1985–87); K. Töth (Hungary; 1985–87); Y. Umezawa (Japan; 1987–91); E. Wang (China; 1987–91); National Representatives: G. Batley (Australia; 1985–89); A. Bond (Australia; 1989–91); B. Gilbert (Belgium); W. Purdy (Canada; 1985–87); H.-Y. Chen (China; 1990–91); A. Vleck (Czechoslovakia); H. Nielsen (Denmark; 1985–88); H. Kristenson (Denmark; 1988–91); K. Cammann (FRG; 1987–89); H. Monien (FRG; 1985–87); M. L'Her (France; 1985–89); Gy. Farsang (Hungary; 1985–87); E. Linder (Hungary; 1985–87); G. Prabhakara Rao (India; 1985–89); R. Kapoor (India; 1989–91); W. Smyth (Ireland); E. Grushka (Israel); S. Rondinini Cavallari (Italy; 1985–87); T. Mussini (Italy; 1987–91); K. Izutsu (Japan; 1987–91); W. Frankvoort (Netherlands; 1985–87); A. McQuillan (New Zealand; 1987–89); Z. Galus (Poland); J. Galvez (Spain; 1987–89); G. Johansson (Sweden); M. Beren (Turkey; 1985–87); G. Souz (Turkey; 1987–91); A. Covington (UK; 1987–91); H. Thompson (UK; 1985–87); J. Jordan (USA; 1985–87); J. Coetzee (USA; 1987–89); W. Koch (USA; 1989–91); I. Peljac (Yugoslavia).
Chemically modified electrodes: Recommended terminology and definitions (IUPAC Recommendations 1997)

Abstract: Chemically modified electrodes (CMEs) comprise a relatively modern approach to electrode systems that finds utility in (1) a wide spectrum of basic electrochemical investigations, including the relationship of heterogeneous electron transfer and chemical reactivity to electrode surface chemistry, electrostatic phenomena at electrode surfaces, and electron and 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, corrosion protection, and electro-organic syntheses.

Compared with other electrode concepts in electrochemistry, the distinguishing feature of a CME is that a generally thin film of a selected chemical is bonded or coated onto 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.

In this report, we have attempted to identify and define the most widely used terminology in the growing field of CMEs and to recommend a particular term in cases where a multiplicity of terms has arisen over the past several years or where previously defined terms have taken on broadened meanings for the special cases of CMEs. It is expected that additional terms will be added to this lexicon in the future as new research directions evolve.

INTRODUCTION

Chemically modified electrodes (CMEs) comprise a relatively modern approach to electrode systems [1] that finds utility in (1) a wide spectrum of basic electrochemical investigations, including the relationship of heterogeneous electron transfer and chemical reactivity to electrode surface chemistry, electrostatic phenomena at electrode surfaces, and electron and 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, corrosion protection, and electro-organic syntheses.

Compared with other electrode concepts in electrochemistry, the distinguishing feature of a CME is that a generally quite thin film (from a molecular monolayer to perhaps a few micrometers-thick multilayer) of a selected chemical 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 includes, but is more diverse 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. While CMEs can operate both amperometrically (or voltammetrically) and potentiometrically, they are generally used amperometrically, a faradaic (charge transfer) reaction being the basis of experimental measurement or study, whereas ISEs are generally used in potentiometric formats where a phase-boundary potential (interfacial potential difference) is the measured quantity [2]. Gas-sensing electrodes (e.g., for CO₂, NH₃, NO₂) are also potentiometrically based [3] although the oxygen electrode, which functions amperometrically, is an exception [4]. 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 [5]. Enzyme-based 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-
modified 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.

In the following discussion of CMEs, it is important to keep in mind the concept of film homogeneity. The presence of variations in film properties between the interfaces with the electrode and solution can dramatically affect many of the other properties discussed below. While film homogeneity is not a necessity, without this property the others are difficult to estimate and a complete description of the behavior of a CME is difficult, if not impossible, to achieve.

**TERMINOLOGY AND DEFINITIONS**

Several of the terms and definitions recommended in this document appear in the *IUPAC Compendium of Chemical Terminology* [6]. However, because of the unique nature of the processes occurring in the CME films, it has been necessary to modify these terms and definitions to conform to these special cases.

**Chemically modified electrode**—(CME)—an electrode made of a conducting or semiconducting material that is coated with a selected monomolecular, multimolecular, ionic, or polymeric film of a chemical modifier and that by means of faradaic (charge-transfer) reactions or interfacial potential differences (no net charge transfer) exhibits chemical, electrochemical, and/or optical properties of the film.

**Electron transport**—general term for processes by which electrochemical charge is transported through films of chemicals to electrodes, including electron self-exchange (vide infra), electron self-exchange coupled to site diffusion, and conduction by highly conjugated molecular components of the film.

**Coverage**—the area-normalized quantity (see surface excess concentration, \( \Gamma \) [7]), usually given in units of mol/m\(^2\), of a designated kind of chemical site in the chemical film. Coverage must be distinguished as to total coverage present versus the coverage that is electrochemically reactive or accessible on some given timescale.

**Biosensor**—a special type of CME or ISE in which a biochemical recognition process is coupled to an appropriate electrochemical transducer. The electrode surface is modified by the attachment of a biocomponent (e.g., enzyme, antigen/antibody, plant or animal tissue, etc.) which functions as the biological recognition element or biochemical receptor [8].

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

Electrodes are usually chemically modified by one of four approaches:

1. **Chemisorption**—adsorption in which the forces involved are the valence forces of the same kind as those operating in the formation of chemical compounds [6]. The chemical film is strongly and, ideally, irreversibly adsorbed (chemisorbed) onto the electrode surface. This approach usually yields monolayer (or less) coverage. Included in this type of modification are the substrate-coupled self-assembled monolayers (SAMs) in which uncorrelated molecules spontaneously chemisorb at specific sites on the surface of the electrode to form a superlattice [9].

2. **Covalent bonding**—linking agents, such as, e.g., organosilanes or cyanuric chloride, are used to covalently attach from one to several monomolecular layers of the chemical modifier to the electrode surface.

3. **Polymer film coating**—electron-conductive and nonconductive polymer films are held on the electrode surface by some combination of chemisorption and low solubility in the contacting solution or by physical anchoring in a porous electrode. The polymer film can be organic, organometallic or inorganic; it can already contain the desired chemical modifier or that chemical can be added to the polymer in a second, functionalizing step; and can contain the equivalent of a few up to many thousands of monomolecular layers of the chemical modifier. Included in this form of modification are the substrate-decoupled SAMs in which adsorbate molecules are arranged on the electrode surface independently of any substrate structure [9].

4. **Composite**—the chemical modifier is simply mixed with an electrode matrix material, as in the case of an **electron-transfer mediator** (electrocatalyst) combined with the carbon particles (plus binder) of a carbon paste electrode. Alternatively, intercalation matrices such as certain Langmuir-Blodgett films, zeolites, clays and molecular sieves can be used to contain the modifier.
CMEs can also contain multiple chemical modifiers, and sometimes these modifiers and/or the electrode substrate may have a particularly designed spatial configuration. That is, a CME may contain one electrocatalyst that reacts with a substrate or acts as a photodonor or acceptor, and a second one to transport charge between the first catalyst and the electrode. Or, the CME may consist of a substrate coated with two different chemical polymers, the second polymer overlaid on the first to form a bilayer of polymer films. These more complex CMEs may be called microstructured electrodes or integrated chemical system electrodes.

Polymer film-coated electrodes may be further subdivided by the process used to apply the film:

1. **Dip-coating**—this procedure consists of immersing the electrode material in a solution of the polymer for a period sufficient for spontaneous film formation to occur by adsorption. The film quantity in this procedure may be augmented by withdrawing the electrode from the solution and allowing the film of polymer solution to dry on the electrode.

2. **Solvent evaporation**—a droplet of a solution of the polymer is applied to the electrode surface and the solvent is allowed to evaporate. A major advantage of this approach is that the polymer coverage is immediately known from the original polymer solution concentration and droplet volume. (Alternate term: droplet evaporation).

3. **Spin coating**—also called spin casting, a droplet of a dilute solution of the polymer is applied to the surface of a rotating electrode. Excess solution is spun off the surface and the remaining thin polymer film is allowed to dry. Multiple layers are applied in the same way until the desired thickness is obtained. This procedure typically produces pinhole-free thin films.

4. **Electrochemical deposition**—also called redox deposition, this procedure relies on the variation of polymer solubility with oxidation (and ionic) state, so that film formation will occur, often irreversibly, when a polymer is oxidized or reduced to its less soluble state.

5. **Electrochemical polymerization**—a solution of monomer is oxidized or reduced to an activated form that polymerizes to form a polymer film directly on the electrode surface. This procedure results in few pinholes since polymerization would be accentuated at exposed (pinhole) sites at the electrode surface. Unless the polymer film itself is redox active, electrode passivation occurs and further film growth is prevented.

6. **Radiofrequency polymerization**—a polymer-filming method in which vapors of the monomer are exposed to a radiofrequency (RF) plasma discharge. The high energetics of the RF discharge may result in chemical damage, thereby producing unknown functionalities and structural modifications to the polymer.

7. **Cross-linking**—a chemical step designed to couple chemical components of a film on an electrode to impart some desired property to the film such as increased stability, decreased permeability, or altered electron transport characteristics. Cross-linked films are often formed by copolymerization of bifunctional and polyfunctional monomers. Cross-linking may be activated chemically, electrochemically, photolytically, radiolytically, or thermally.

In all of the above cases, the redox moiety (electron-transfer mediator or electrocatalyst) may be bound to the monomer or polymer before application of the film to the electrode, or the polymer film may be derivatized (functionalized) subsequent to film application.

There are several reasons for the appeal of polymer modification: immobilization is technically easier than working with monolayers; the films are usually more stable; and, because of the multiple layers of redox sites, the electrochemical responses are larger. Questions remain, however, as to how the electrochemical reactions of multimolecular layers of electroactive sites in a polymer matrix occur, e.g., mass transport and electron transfer processes by which the multilayers exchange electrons with the electrode and with reactive species: molecules and ions in the contacting solution [1,10]. Much of this uncertainty results from a lack of sufficient knowledge about the structure and properties of polymer films and the morphological changes that they undergo when subjected to various chemical, electrochemical and physical processes during use.

Electrocatalysis at a modified electrode is usually an electron transfer reaction between the electrode and some solution substrate which, when mediated by an immobilized redox couple (i.e., the mediator), proceeds at a lower overpotential than would otherwise occur at the bare electrode. This type of mediated electrocatalysis process can be represented by the scheme: 

© 1997 IUPAC, Pure and Applied Chemistry 69, 1317–1323
In this scheme, the subscripts s and m designate the solution and membrane phases, respectively. The substrate, S, which is irreversibly (or quasi-reversibly) reduced at the bare electrode, is transported across the polymer film-solution interface (partition coefficient, $K_p$) and diffuses into the polymer film membrane (diffusion coefficient, $D_{s/m}$). The electrocatalyst or mediator, R/O, undergoes heterogeneous electron transfer (rate constant $= k_1$) at the electrode surface and charge propagation through the polymer film is described by a rate given by the charge-transport diffusion coefficient, $D_{ct}$ (the symbol $D_e$ is not recommended). The mediator undergoes homogeneous electron transfer (rate constant $= k_2$) with the substrate in the polymer film (vide infra).

The charge-transport diffusion coefficient may be composed of one or more of the following components:

1. **Self-exchange reaction**—electron transfer between neighboring electrocatalytic redox sites in the polymer matrix [11] (also called the electron-hopping mechanism).

2. **Site diffusion**—random motion of the polymer chains brings the attached redox sites into close proximity, thereby allowing electron transfer to occur.

3. **Counter-ion diffusion**—to maintain electroneutrality in the polymer film, counter ions (often with associated solvent) must diffuse into or out of the polymer matrix to compensate for the charge propagation in the film.

4. **Electromigration**—in contrast to a solution containing supporting electrolyte, the ionic resistivity of the polymer film creates an uncompensated resistance, and thus an $iR$ drop across the film, that results in an electric field gradient in the polymer film. Depending on the polarity of this field and the charge on the counter ions and/or substrate species (if ionic), mass and charge transport may be enhanced or diminished by the electric field, resulting, for example, in non-Cottrell behavior in chronoamperometric experiments.

5. **Ion pairing**—kinetic control of charge transport may occur due to coulombic interactions [12] between immobile redox sites and electroinactive counter ions. The mobile counter ion thus controls the charge transport rate through its ion-pairing association constant rather than by its own mobility [10].

Within the film, if the substrate and charged mediator react; this is the electrocatalytic reaction. This reaction may be a simple homogeneous electron transfer or cross-exchange reaction, regenerating the oxidized form of the mediator and forming the reduction product P. If the heterogeneous electron transfer rate between the mediator and the electrode is fast, then the reaction with substrate is turned on at the surface formal potential of the mediator couple which is the potential at which the charged form of the mediator begins to be generated. This type of mediated outer-sphere electrocatalysis is termed redox catalysis.

A more complex type of electrocatalysis, called chemical catalysis, occurs when the reaction between substrate and mediator is an inner-sphere reaction and yields a chemical adduct or some other electroactive intermediate. In this case, the potential for electrocatalysis can differ from the formal potential of the mediator, being instead, for example, that of the mediator-substrate adduct.

The location of the reaction between mediator and substrate in the polymer film can vary depending on the relative kinetics of the permeability ($K_pD_{s/m}$) of the substrate into the polymer film, of the electron charge transport ($D_{ct}$), and of the mediator-substrate reaction itself. The reaction zone can be localized at
the polymer/solution interface, at the polymer/electrode interface, or distributed throughout the interior of the polymer film [13,14].

The application of the polymer-film electrocatalysis approach can be further extended to photoelectrochemical reactions at modified semiconductor [6] electrodes. In such cases, the immobilized substance(s) may serve several functions: mediation of the redox processes, photosensitization [6] of the semiconductor, and photoanodic corrosion protection.

Preconcentration (preferential uptake) of substrate or analyte ions/molecules is another area of utility of CMEs [15,16]. In practice, the electrode surface is modified by the judicious choice of a reagent capable of selectively, and nonelectrolytically, accumulating the analyte of interest. The mechanism of this process is determined by nature of the reactivity of the modifying moiety, and the most common preconcentration mechanisms are usually based on solubility (e.g., hydrophobic interactions), coordination, or electrostatic phenomena (e.g., ligand- or ion-exchange interactions). In electroanalysis, accumulation of the analyte in the chemical modifier leads to higher sensitivity and may also provide improved selectivity.

Other relevant polymer-film properties are:

1. **Stability**—resistance to degradation or dissolution in aqueous and nonaqueous solvents and in other hostile media, and the strength of the bonding between (a) the redox sites and the polymer matrix and (b) the polymer film and the electrode surface.
2. **Permeability**—the ease with which various species penetrate the polymer matrix. This includes not only the permeability of the polymer to the reaction substrate, noted above, but also the permeability of the polymer to the reaction product(s) and to ionic components, such as the supporting electrolyte. These parameters, among others, determine the uncompensated resistance within the film during the passage of current, as well as the time for electrochemical charging of sites within the film. The permeability of the film to solvent is also important as this affects transport properties of the other components. Lack of permeability to solvent or ionic species may cause a film to act as a passive barrier even though it contains electrochemically reactive sites. Some polymer films exhibit permselectivity (selective permeability) [6] which may be of analytical utility by providing size or charge discrimination among species and also by preventing fouling of the electrode surface by sample matrix components, e.g., proteins in biological fluids [16].
3. **Site population**—this is the concentration of some designated chemical sites within the polymer film and is the ratio of coverage to film physical thickness. Concentration is often difficult to specify accurately since the solvent-swollen thickness of very thin films is difficult to assess, and because the total coverage may in some cases be larger than the electrochemically reactive coverage. The site concentration may nonetheless have important effects on the charge transport rates and consequently the magnitude of the faradaic current.
4. **Conductivity**—the polymer film may transport electrons (propagate charge) by localized site-site hopping (electron self-exchange) or by an electron delocalization mechanism when highly conjugated polymer chains are present. These conduction modes are termed redox conduction and electronic conduction, respectively, and the latter types of polymers are often termed (electronically) conducting polymers. Additional conduction mechanisms arise in heterogeneous CMEs where conducting materials are embedded in non- or less-conducting matrices. In polymers where charge is conducted by ionic, as well as redox/electronic, mechanisms, these processes are coupled by local electroneutrality in any spherical region large compared with a single charged species [17].

**SUMMARY**

In this report, we have attempted to identify and define the most widely used terminology in the growing field of chemically modified electrodes (CMEs) and to recommend a particular term in cases where a multiplicity of terms has arisen over the past several years or where, as in the case of reference 6, previously defined terms have taken on broadened meanings for the special cases of CMEs. It is expected that additional terms will be added to this lexicon in the future as new research directions evolve.
REFERENCES


