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Sensors and biosensors based on clay-modified electrodes — new trends

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Abstract

Clay-modified electrodes (CLMEs) have received attention in the development of electrochemical sensors and biosensors. This article reviews the use of CLME for these electroanalytical purposes. It includes an introduction to the structure of cationic and anionic clays, an overview of electron transfer occurring at CLME, and of the different modes of preparation of CLME. The analytical applications reported for CLME range from the preconcentration method applied to the detection of cationic species (i.e., metal cations) or organic molecules (i.e., water pollutants and drugs), to electrocatalytic sensors involving intercalated redox mediators in the electrochemical detection process, and finally to amperometric and potentiometric biosensors. Several enzymes have been immobilized within clay matrices and amperometric biosensors based on CLME are presented following the three modes of detection referred to as first, second, and third generation of biosensors, depending on the nature of the enzymes.
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Keywords: Clay-modified electrodes; Electroanalysis; Electrochemical biosensors; Layered double hydroxides; Redox mediator; Enzyme

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Abbreviations: AA, ascorbic acid; ABTS, 2,2′-azinobis 3-ethylbenzothiazoline-6-sulfonate; AlDH, alcohol dehydrogenase; BSA, bovine serum albumin; Cc, cobaltocenium; CE, cholesterol esterase; CEC, cationic exchange capacity; CO, cholesteroloxidase; CPE, carbon paste electrode; CV, cyclic voltammetry; DDAB, didodecyldimethylammonium; DHB, 3,4-dihydroxybenzaldehyde; DPV, differential pulse voltammetry; EQCM, electrochemical quartz crystal microbalance; FAD, flavin-adenine dinucleotide; Fc, ferrocene; Fre, flavin reductase; GA, glutaraldehyde; GOD, glucose oxidase; GCE, glassy carbon electrode; HRP, horseradish peroxidase; ITO, indium tin oxide; LaDH, lactate dehydrogenase; LDHs, layered double hydoxides; MG, methylene green; MP, maltose phosphorilase; MR, mutarotase; MV^{2+}, methylviologen; NADH, nicotinamide adenine dinucleotide; PGE, single use pencil graphite electrode; PISE, potentiometric Ion Sensitive Electrode; PMMA, polymethyl methacrylate; PPD, poly(o-phenylenediamine); PPO, polyphenol oxidase; Pr, protein; PS, organosilasesquioxane pillared laponite; Py, lead ruthenate pyrochlore ($Pb_2Ru_{2-x}Pb_xO_{7-y}$); SPE, screen-printed electrode; SWV, square wave voltammetry; TCA, trichloroacetic acid; TTF, tetrathiofulvalene; XO, xanthine oxidase.

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1. Introduction

A "chemical sensor is a small device that, as the result of a chemical interaction or process between analyte and the sensor device, transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal" (Stetter et al., 2003). All chemical sensors contain two basic components: a chemical recognition system (receptor) and a transducer. Biosensors are chemical sensors in which the recognition system uses a biological mechanism instead of a chemical process. A transducer transforms the response measured at the receptor into a detectable signal. Among all the chemical sensors reported in the literature, electrochemical sensors are the most attractive because of their remarkable sensitivity, experimental simplicity, and low cost. The signal from the transducer can be a current (amperometry), a voltage (potentiometry), or impedance/conductance changes (conductimetry).

Chemical layers can be used for importing a high degree of selectivity to electrochemical transducers. Chemically modified electrodes (CMEs) provide one approach to the development of these analytical devices. CMEs are important constituents of both immobilized reagent systems and sensitive layers. In trace analysis, during the accumulation reaction, CMEs preconcentrate the analyte into a small volume on the electrode, allowing lower concentrations to be measured than possible in the absence of a preconcentrated step (adsorptive stripping voltammetry). CME can also be applied to electroanalysis because of their own electrocatalytic properties and/or their capacities to immobilize electrocatalytic or biocatalytic (enzyme) reagents that improve the sensitivity and selectivity of the detection step.

The majority of modified electrodes can be obtained by chemisorption, covalent bonding, and film deposition (Murray, 1992). Among the wide range of electrode modifiers, inorganic materials, such as zeolites, silica-based hybrid materials, and clays, have attracted the attention of electrochemists, in particular for their analytical applications (Walcarius, 1996, 1998, 2001; Navrátilová and Kula, 2003).

Clays can be divided into two main classes: cationic clays that have negatively charged alumino silicate layers; and anionic clays, with positively charged hydroxide layers. The neutrality of these materials is ensured by ions, cations, or anions, depending on the clay type, in the interlayer space that balances the charge. Cationic clays are among the most common minerals on the earth's surface. They have been used for centuries to produce ceramics. Furthermore, they find applications in pharmacy, cosmetics, catalysts, adsorbents, and ion exchangers (Vaccari, 1998, 1999). These last applications are particularly useful for the development of electrochemical sensors. Most clays used at clay-modified electrodes (CLME) are Smectite clays. Their names and formula are given in Table 1 (Newman and Bown, 1987; Van Olphena and Fripiat, 1979). They can serve as matrices for electroactive ions because they are usually able to incorporate ions by an ion-exchange process, like polymeric ionomers. Moreover, adsorption of proteins on clay mineral surfaces plays a very important role not only in fields related to agricultural and environmental sciences, but also in the development of biosensors (Gianfreda et al., 2002). Layered

Table 1
Composition of clay types used at clay-modified electrodes

Clay type	Name	Idealized formula	Charge (mEq/g)
Cationic, 2:1 dioctahedral	Montmorillonite	$(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2\ (Na_x^+, nH_2O)$	0.60–1.00
	Nontronite	$Fe_2^{3+}\ (Si_{4-x}Al_xO_{10})(OH)_2\ (Na_x^+, nH_2O)$	0.76
Cationic, 2:1 trioctahedral	Hectorite	$(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2\ (Na_x^+, nH_2O)$	0.44
	Laponite (synthetic Hectorite)	$(Mg_{5..5}Li_{0.5})Si_4O_{10}(OH)_2\ (Na_x^+, nH_2O)$	0.73
	Vermiculite	$Mg_3(Si_{4-x}Al_xO_{10})(OH)_2\ (Na_x^+, Ca_{x/2}^{2+}, nH_2O)$	1.20–2.00
Sepiolite		$(Mg_{8-y-z}R_y^{3+}{}_3)(S_{12-x}\ R_x^{3+})(OH)_4(OH_2)_4R_{x-y+2}^{2+}\ (H_2O)_8$	
Anionic	Hydrotalcite	$[Mg_6Al_2(OH)_{16}]CO_3.4H_2O$	3.3
	Layered Double Hydroxides (LDHs)	$[M_{1-x}^{II}M_x^{III}(OH)_2]X, nH_2O$	1.0–1.5
	[Zn$_3$–Al–Cl]	$[Zn_3Al(OH)_8]Cl, 2H_2O$	2.32
	Friedel's salt	$CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$	

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