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Tetrabutylammonium-modified clay film electrodes: Characterization and application to the detection of metal ions



Adela Maghear^{a,d,1}, Mihaela Tertiş^{a,b,1}, Luminița Fritea^a, Iuliu O. Marian^b, Emil Indrea^c, Alain Walcarius^d, Robert Săndulescu^{a,*}

^a Analytical Chemistry Department, Faculty of Pharmacy, "Iuliu Hațieganu" University of Medicine and Pharmacy, 4 Louis Pasteur Street, 400349 Cluj-Napoca, Romania

^b "Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Street, 400028 Cluj-Napoca, Romania

^c National Institute for R&D of Isotopic and Molecular Technologies, 65-103 Donath Street, 400295 Cluj-Napoca, Romania

^d Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564, CNRS – Université de Lorraine, 405 rue de Vandoeuvre, F-54600 Villers-lès-Nancy, France

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ABSTRACT

This work describes the preparation and characterization of smectite clay partially exchanged with tetrabutylammonium ions (TBA⁺) and its subsequent deposition onto glassy carbon electrode (GCE) for application to the preconcentration electroanalysis of metal ions (Cd, Pb, and Cu). Such partial exchange of TBA⁺ induces the expansion of the interlayer region between the clay sheets (as ascertained by XRD) while maintaining its ion exchange capacity, which resulted in enhanced mass transport rates (as pointed out by electrochemical monitoring of permeability properties of these thin (organo)clay films on GCE). This principle was applied here to the anodic stripping square wave voltammetric analysis of metal ions after accumulation at open circuit. Among others, detection limits as low as 3.6×10^{-8} M for copper and 7.2×10^{-8} M for cadmium have been achieved.

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1. Introduction

Clay-modified electrodes (CLMEs) have been developed from few decades ago [1–3], but they still represent a notable field of interest, especially for their applications in electroanalysis, as discussed in some reviews [3–6] and illustrated in recent research papers where CLMEs have been used as sensors or biosensors (see examples, from our group [7–9] and from those of Ngameni [10–17], Mousty [18,19], or some others [20–22]). Clay minerals used as electrode modifiers are primarily (but not only) phyllosilicates-layered hydrous aluminosilicates. An important characteristic of those minerals is their interlayer distance which depends on the number of intercalated water and exchangeable cations within the interlayer space [4]. They also exhibit attractive properties such as a relatively large specific surface area, ion exchange capacity, and the ability to adsorb and intercalate some organic species. Smectites have been mostly used for CLMEs preparation in thin layer configuration, especially

montmorillonite (MMT), due to a high cation exchange capacity (typically $0.80\text{--}1.50$ mmol g⁻¹) and its thixotropy likely to generate stable and adhesive clay films on electrode surfaces [4,6].

Keeping in mind that clays are insulating materials, their use in electrochemistry thus requires a close contact to an electrode surface, which can be achieved via either the dispersion of clay powders in a conductive composite matrix (e.g., carbon paste electrode [23]) or the deposition of clay particles as thin films on solid electrode surfaces. An advantage of the clay film modified electrodes is that they are binder-free, thanks to the particular platelet morphology of clay particles bringing them self-adhesive properties toward polar surfaces [5], which ensure a better interaction with most electrode materials and, consequently, a more durable immobilization. Clay films can be attached to a solid electrode surfaces by physical means (through solvent casting, spin-coating, or layer-by-layer assembly [5,6,24]), or electrophoretic deposition [25], by covalent bonding (via silane or alkoxy silane coupling agents) [26,27], or, more recently, in the form of clay–silica composite films [28]. At the beginning, CLMEs were mainly prepared from bare (unmodified) clay materials [5,6] but recent advances have been mainly based on organically-modified clays (obtained either by intercalation or grafting of organic moieties in the interlayer region of the clay [29–32]) because they enable to

* Corresponding author. Tel.: +40 264 582441, +40 745 770514.

E-mail address: rsandulescu@umfcluj.ro (R. Săndulescu).

¹ Equal contribution.

tune, control and extend the clay properties, resulting therefore to better analytical performance in terms of selectivity and sensitivity [10–17].

Dealing with sensitivity, preconcentration electroanalysis at modified electrodes (in which the analyte is firstly accumulated at open circuit and then electrochemically detected) has proven to be a powerful method to improve the performance of electrochemical sensors. In this respect, the ion exchange capacity of clays and the binding properties of organoclay have been exploited for the detection of metal ions using CLMEs (see examples in reviews [1,4]). Till now, however, very few examples are based on the use of intercalated organoclay materials for that purpose [11,16], in spite of the simpler modification procedure for intercalation than for grafting for instance (which requires the use of particular organoalkoxysilane reagents [10,15]). Here, we have thus examined the interest of CLMEs based on clay particles intercalated with tetrabutylammonium (TBA^+) moieties for the preconcentration electroanalysis of some metal ions (*i.e.*, Cd^{2+} , Pb^{2+} and Cu^{2+}). The choice of this tetraalkylammonium intercalation reagent was motivated by at least two features: (1) TBA^+ ions can be easily intercalated in the interlayer region of smectite clays by ion exchange [33], and (2) it modifies the packing configurations in the interlayer of the clay thus influencing the sorptive properties of the organoclay [34], notably with respect to adsorption of metal ions such as Cu^{2+} or Cd^{2+} [35,36].

The present study describes the deposition of partially TBA^+ -modified clay particles (montmorillonite-rich natural clay from Romania) onto a glassy carbon electrode surface, subsequently covered with a dialysis tubing cellulose membrane, a configuration ensuring fast mass transport for analytes from the solution through the film to the electrode surface. The modified electrode was applied to the detection of some metal ions chosen as relevant biological and environmental contaminants (Cd^{2+} , Pb^{2+} and Cu^{2+}).

2. Experimental

2.1. Chemicals, reagents and clay materials

NaNO_3 (99%, Fluka), HCl (37%, Riedel de Haen), and tetrabutylammonium bromide (TBAB, 99%, Sigma) were used as received without further purification. The redox probes employed for permeability tests were of analytical grade: ferrocene dimethanol ($\text{Fc}(\text{MeOH})_2$, Alfa Aesar); potassium hexacyanoferrate(III) ($\text{K}_3\text{Fe}(\text{CN})_6$, Fluka); and hexaammineruthenium chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, Sigma-Aldrich). Single-component and multicomponent cation solutions were prepared daily by diluting standardized mother solutions (comprised of 1000 mg/l each metal ion, from Sigma-Aldrich). These standards were also used to certify copper(II) solutions prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.05 M HNO_3 , lead (II) solutions prepared from $\text{Pb}(\text{NO}_3)_2$ and 0.5 M HNO_3 and cadmium(II) solutions prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.5 M HNO_3 , Sigma-Aldrich, which were used to prepare diluted solutions for preconcentration studies (final pH in the electrolyte was 5.5 if not stated otherwise). The electrolyte employed was 0.1 M NaNO_3 . All solutions were prepared with high purity water ($18 \text{ M}\Omega \text{ cm}^{-1}$) from a Millipore milli-Q water purification system.

The clay sample used in this study was a natural Romanian clay from Valea Chioarului (Maramureş County), consisting mainly of MMT, with minor amounts of quartz. Its physico-chemical characterization is provided elsewhere [9]. The structural formula is $(\text{Ca}_{0.06}\text{Na}_{0.27}\text{K}_{0.02})_{\Sigma=0.35}(\text{Al}_{1.43}\text{Mg}_{0.47}\text{Fe}_{0.10})_{\Sigma=2.00}(\text{Si}_{3.90}\text{Al}_{0.10})_{\Sigma=4.00}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. It is characterized by a surface area (N_2 , BET) of $190 \text{ m}^2 \text{ g}^{-1}$. Only the MMT-rich fine fraction of the clay ($< 1 \mu\text{m}$, as collected by sedimentation according to Stockes law, after the raw clay was suspended in water, ultrasonicated for about 15 min and

allowed to settle, centrifugation and ultracentrifugation of the supernatant phase) was used here. This fine fraction has a cation exchange capacity (CEC) of $0.78 \text{ mequiv g}^{-1}$ and was used before as template for an amperometric biosensor for acetaminophen detection [8]. Its XRD diffractogram showed a high content of MMT (with its characteristic peaks at 2θ : 6.94° ; 19.96° ; 21.82° ; 28.63° ; 36.14° ; and 62.01°) and also confirmed the almost negligible presence of other minerals.

2.2. Apparatus and characterization procedures

Electrochemical experiments were carried out using a PGSTAT-12 potentiostat (EcoChemie) equipped with the GPES software. A conventional three electrode cell configuration was employed for the electrochemical measurements. Film modified GCEs were used as working electrodes, with an $\text{Ag}/\text{AgCl}/\text{KCl}$ 3M reference electrode (Metrohm) and a platinum wire as reference and counter electrode. Cyclic voltammetry (CV) was carried out correspondingly in 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, and 5 mM $\text{Fc}(\text{MeOH})_2$ (in 0.1 M NaNO_3). CV curves were typically recorded in multisweep conditions at a potential scan rate of 20 mV s^{-1} and used to qualitatively characterize accumulation/rejection phenomena and mass transport issues through the various films.

Accumulation–detection experiments were also performed using copper(II), lead(II), and cadmium(II) as model analytes. Typically, open-circuit accumulation was made from diluted cations solutions (5×10^{-7} – 10^{-6} M) at pH 5.5 and voltammetric detection was achieved after medium exchange to a cation-free electrolyte solution (0.1 M NaNO_3) by square wave voltammetry (SWV), at a scan rate of 5 mV s^{-1} , a pulse amplitude of 50 mV and a pulse frequency of 100 Hz.

The CNH elemental analysis of clay and organoclay materials was performed using an Elementar Vario Micro Cube, with the following experimental conditions: combustion temperature 950°C ; reduction temperature 550°C ; He flow 180 ml/min; O_2 flow 20 ml/min; and pressure 1290 mbar.

The film structure was characterized by X-ray diffraction (XRD), FTIR and Raman spectroscopy. XRD measurements were performed using a BRUKER D8 Advance X-ray diffractometer, with a goniometer equipped with a germanium monochromator in the incident beam, using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range 15 – 85° . The FTIR spectra were measured on a Jasco FT/IR-4100 spectrophotometer equipped with Jasco Spectra Manager Version 2 software (550 – 4000 cm^{-1}). The Raman spectra were acquired with a confocal Raman microscope (Alpha 300R from WiTec) using a WiTec Control software for data interpretation (1000 – 3600 cm^{-1} , resolution $> 0.5 \text{ cm}^{-1}$).

Electrochemical impedance spectroscopy (EIS) was used to characterize the electron transfer properties of the modified electrodes. The Nyquist plots were recorded with an Autolab potentiostat equipped with a FRA2 module and 4.9 version software.

2.3. Clay modification with TBAB

A MMT sample (10 g, particle size $< 1 \mu\text{m}$) was suspended in ultrapure demineralized water (clay concentration in water 4%). A quantity of Na_2CO_3 equivalent to 100 mequiv Na_2CO_3 per 100 g clay was then added in the clay suspension and stirred for 30 min at 97°C . An aqueous solution of TBAB (corresponding quantitatively to 1.1 times montmorillonite cation exchange capacity ($\text{CEC}_{\text{MMT}} = 0.78 \text{ mequiv g}^{-1}$); 0.85 mequiv g^{-1} of TBAB), was then added and the suspension was stirred for 30 more minutes at room temperature. The obtained solid was separated by centrifugation and washed until it was free of any residual Br^- . The organoclay material was then dried for 48 h at 60°C . When necessary, TBAB was partially solvent-extracted in an ethanol

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