Electrochimica Acta 54 (2009) 4237–4244

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

H_2O_2 determination at iron-rich clay modified electrodes

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ARTICLE INFO

Article history:
Received 17 November 2008
Received in revised form 23 February 2009
Accepted 23 February 2009
Available online 9 March 2009

Keywords:
Clay modified electrode
Hydrogen peroxide
Hemoglobin
Methyl viologen
Structural iron
Amperometric sensors

ABSTRACT

The electrochemical properties of natural or synthetic ferruginous clays, nontronite, montmorillonite and saponite, were studied by cyclic voltammetry and impedancemetry. Clay modified electrodes were then tested for the reduction of hydrogen peroxide under different conditions: in acidic medium without redox mediator, in phosphate buffer solutions (pH 7 or 8) with a redox cation (methyl viologen, MV^{2+}) or a biomolecule (hemoglobin, Hb) absorbed within the clay coating. In all cases, the presence of iron species in the octahedral lattice of the clays enhanced the electrocatalytic reduction currents of H_2O_2. The sensitivities of H_2O_2 calibration curves were 0.23, 54 and 132 mA/M cm^2 for Nont, MV^{2+}-Nont and Hb-Nont modified electrodes, respectively.

1. Introduction

Smectites are 2:1 phyllosilicates with a layer structure consisting of an octahedral sheet sandwiched between two tetrahedral siliceous sheets. Octahedral sheet is dominantly occupied by trivalent cations (dioctahedral smectites: i.e. montmorillonite, nontronite) or divalent cations (trioctahedral smectites: i.e. saponite). In tetrahedral sheets the dominant cation is Si^{4+}, in octahedral sheets the cations are usually Al^{3+}, Mg^{2+}. Cations such as Fe^{3+} or Fe^{2+} can occupy either tetrahedral or octahedral sites. Isomorphic substitutions within octahedral and/or tetrahedral sheets lead to negative charges of the layers compensated by interlayer cations. Parameters such as layer charge, charge location, nature of the interlayer cations affect smectite hydration ability and swelling behavior [1].

Over the past decades, it has been demonstrated that the presence of iron, as trace element in the crystal structure of natural smectite clays, greatly influences their physical and chemical properties with subsequent consequences in agriculture, environment or industrial processes in which clays are involved. These Fe atoms are suggested to be involved in electron transfer occurring at the clay surface, with adsorbed aromatic molecules or pesticides, for example.

Electrochemical techniques are useful to monitor the electron transfer occurring at the clay surface [2]. However, few papers report on the direct reduction of iron in the crystal lattice of the clays. Villemure's group reported that direct reduction of metal ions is possible when using iron-rich synthetic clays [3,4]. Wang's group has shown direct electron transfer from iron sites in natural clays in acidic solution [5]. The redox activity of iron in clays is easily evidenced with intercalated redox mediators or photo-sensibilizers [5,6].

This trace element can affect the response of clay modified electrodes (CMEs) with an electrocatalytic behavior. For instance, Oyama and Anson reported that structural iron sites present in the natural montmorillonite could mediate the reduction of hydrogen peroxide [7]. This proposed electrocatalytic activity of iron in CMEs has always involved adsorbed electroactive species as charge mediators ($Ru(NH_3)_6^{2+}$, $Fe(bpy)_3^{3+}$, methyl viologen) [7–9]. Photochemical and electro-luminescence experiments confirmed that iron species contained in the natural nontronite catalyzed efficiently the decomposition of H_2O_2 [10–13]. In these cases also, photoreactive substances play the role of electron relay [10,11]. However, these CMEs have never been used for the development of sensitive analytical sensors of H_2O_2.

On the other hand, hydrogen peroxide detection has been performed by using hemoglobin (Hb) as a biocatalyst immobilized at the CME surface [14,15]. Indeed, several papers in the literature

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doi:10.1016/j.electacta.2009.02.078

report the direct electron transfer occurring between electrode surface and heme proteins, immobilized on pure [16–19] or hybrid montmorillonite [15,20,21]. However, the possible role of structural iron to enhance electrocatalytic properties of heme proteins has never been investigated.

In the present work, the electrochemical properties of ferruginous clays, one natural and two synthetic, were studied by cyclic voltammetry and impedancemetry. A synthetic montmorillonite (MS) containing non iron impurities was used as a reference. Our final goal is devoted to a basic understanding of the role played by structural iron in electron transfer occurring at the clay surface and to show the possible analytical applications employing the three clay materials as electrode modifiers. The modified electrodes prepared with these clays have been tested for the reduction of H_2O_2 under different conditions:

(a) in acidic medium without redox mediator,
(b) in phosphate buffer solution (pH 8) with adsorbed methyl viologen (MV^{2+}) as an electron shuttle,
(c) in phosphate buffer solution (pH 7) with absorbed hemoglobin as a biocatalyst.

The resulting CMEs were characterized by cyclic voltammetry with and without the presence of H_2O_2 and, finally, the calibration curves were recorded under amperometric conditions. The results are discussed in relation to the clay properties, in particular the iron amount present in their structure and its structural site.

2. Experimental

2.1. Clays and products

The natural ferruginous smectite clay used here was the natural nontronite from Garfield Washington (NontG) purchased from Cay Minerals Repository (University of Missouri, Columbia). It was purified and exchanged with sodium by a conventional exchange reaction. The clay was dispersed in 1N NaCl, stirred for 24 h, and then centrifuged. This procedure was repeated five times; afterwards the clay was washed with water until a negative chloride test was obtained. The final fraction was recovered by centrifugation and dried.

A synthetic montmorillonite presenting Fe(III) only in the octahedral sheet (MSF) and a synthetic montmorillonite containing non iron impurities (MS) were kindly offered by Jocelyne Brendle (LMPC UMR 7016, Mulhouse). Jean-Louis Robert (ISTO UMR 6113, Orléans) has prepared the synthetic saponite (SapSF) which has Fe(III) only in the tetrahedral sheet. All these synthetic clays were used as received. The clay compositions and their cationic exchange capacities and BET surfaces have been communicated by our colleagues or found in the literature [22,23]. The concentration (mmol/g) of iron and the charge distribution have been calculated from the clay formula [24]. All these data are indicated in Table 1.

Hydrogen peroxide (H_2O_2) and hydroquinone (HQ) solutions (from Sigma–Aldrich) were freshly prepared before being used. Methyl viologen (MV^{2+} $2PF_6$) was synthesized in our laboratory [25]. Hemoglobin from bovine blood (Sigma–Aldrich) was used without further purification. Phosphate buffer solutions (PBS) were prepared with sodium phosphate dibasic ($Na_2HPO_4{\cdot}10H_2O$) and sodium monobasic NaH_2PO_4 from Acros. Acid solution was prepared with sodium sulphate Na_2SO_4 and H_2SO_4 from Acros.

2.2. Instrumentation

Hydrodynamic clay particle sizes were measured by photocorelation spectroscopy with a Zetasizer nanoZS Malvern instrument. The thicknesses of dried films formed with 40 μg of clay were measured by a surface profilometer Alpha-Step IQ. Transmission electron microscopy (TEM) images were taken using a Hitachi 7650 microscope at an acceleration voltage of 80 kV. Samples were dispersed in ethanol and then one droplet of the suspension was applied to a 400 mesh holey carbon-coated copper grid and left to dry in air.

Cyclic voltammetry and chronoamperometry experiments were carried out with a potentiostat EA161 (EDAQ) connected to a thermostated cell (20 ml) with a three-electrode system, including an Ag/AgCl reference electrode, a platinum auxiliary electrode and a glassy carbon disk electrode (GCE) modified with clay films as working electrode. Rotating disk electrode (RDE from Radiometer) was utilized for chronoamperometry, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (IES). The electrolyte solution was degassed by bubbling with argon for at least 30 min before to start the measurements.

Impedance measurements (IES) were carried out with a potentiostat Autolab PGSTAT 100 Eco-Chemie. A sinusoidal potential modulation with a root mean square amplitude of 5 mV was superimposed on the formal potential of HQ at 0.4 V/ECS with a frequency ranging from 50,000 to 0.1 Hz; the rotation speed of RDE was fixed at 500 rpm. A ZView software (Scribner Associates Inc.) was used to simulate the data thus obtained using an appropriate equivalent electrical circuit.

2.3. Procedure

Prior to use, the glassy carbon electrodes were polished with alumina particles (0.05 μm), then cleaned by ultrasonication in water and ethanol and finally rinsed with water and dried. Clay films were prepared by dropping a known volume of clay colloids (2 mg/ml) prepared in deionized water onto a clean electrode and then dried under ambient conditions. Generally, 20 or 40 μg of clays were cast on GCE ($A = 0.07\ cm^2$) for cyclic voltammetry or impedance experiments.

Calibration curves were obtained by recording steady state chronoamperograms (i_{lim} *vs* time) with a rotating GC disk electrode ($A = 0.196\ cm^2$) at 500 rpm. Successive injections of concentrated stock H_2O_2 solution in the batch cell were performed with a syringe. The amount of clay deposited onto the electrode surface was optimized to obtain the best sensor performances with a good stability. In acid solution (pH 2), H_2O_2 calibration curves were recorded using (40 μg) Fe–clay coated electrodes. In phosphate buffer solutions (pH 7 or 8), with clay modified electrodes contained two types of

Table 1
Physical characteristics of clays.

Clay	Composition	PS (nm)	CEC (meq/100 g)	BET (m^2/g)	Iron (site)[a] (mmol/g)	Charge[a] (mol/unit cell)	
						O	*T*
NontG	$(Si_{7.22}Al_{0.78})(Fe_{3.64}Al_{0.32}Mg_{0.04})O_{20}(OH)_4Na_{0.82}$	750	104	57	4.2 (*O*)	−0.04	−0.78
MSF	$Si_8(Al_3Fe_{0.34}Mg_{0.66})O_{20}(OH,F)_4Na_{0.66}$	600	–	142	0.41 (*O*)	−0.66	
MS	$Si_8(Al_{3.2}Mg_{0.8})O_{20}(OH,F)_4Na_{0.8}$	550	90	60	0	−0.80	
SapSF	$(Si_{6.8}\ Fe_{0.8}\ Al_{0.4})Mg_6O_{20}(OH)_4Na_{1.2}$	635	148	–	1.0 (*T*)		−1.2

[a] Calculated from clay formula [24].