Organoclay modified electrodes: The influence of acid activation and pillaring on the electrochemical activity of montmorillonite

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Smectic clay suspensions have been used to prepare clay-modified electrodes (CMEs) presenting unique properties (high surface area and cation exchange capacity, swelling and intercalation as well as chemical and mechanical stability) [1-3]. These properties provide new patterns of reactivity to incorporate reactants on CMEs. The use of CMEs is limited to positively charged species, since anionic species cannot be adsorbent on the clay film. However, cationic surfactants adsorb easily on the clay and built up a positive bilayer. Thus, when a CME has been pre-exchanged with cationic surfactants such as cetyltrimethylammonium bromide (CTAB), it can act as an excellent collector of anionic species from dilute solutions [4,5].

In the present study, we examine the electrochemical activity of a natural clay (M) treated with CTAB, before and after acid activation and pillaring, We compare the sensitivity of the corresponding montmorillonite (ME), acid-activated (AME), pillared (PME) and pillared acid activated (PAME) montmorillonite modified electrodes in aqueous solutions of anionic red-ox active species.

The results summarized on Table 1, show that the CTA^+ pre-exchanged acid activated clay presents the highest ability to incorporate anionic species. Pillaring of the clay matrix decreases drastically the incorporation of anionic species, but acid activation of clay matrix before pillaring slightly increases the quantity of adsorbed anions. The ratio I_{pa}/I_{pc} shows that the AME and PAME lose more easily the incorporated species, which may be due to the acid activated clay matrix. In addition, the ME, AME, and PME can adsorb anionic species form solutions as dilute as 10^{-5}M $[Fe(CN)_6]^{4-}$, although the PAME is electroactive in more dilute solutions ($5x10^{-6}$M $[Fe(CN)_6]^{4-}$).

It is well known that acid activation and pillaring processes reduce CEC, but increase surface area and acidity of the parent clay. In addition, a number of electroactive species are leached out of the clay film when the electrodes are transferred in pure supporting electrolyte [6-7]. These reasons support the idea that the interaction of surfactants and anionic species in the clay material has an electrostatic character [8]. Its origin is probably the formation of ion pairs between the hydrophobic organoclay framework and the anionic red-ox active species. Thus, the ion pair mechanism, well established in the case of cationic species incorporated into a CME [3], can now be extended to organoclay modified electrodes.

The more complex surface characteristics of the acid activated clay matrix and the high acidity favour the formation of ion pairs. In fact, the acidity of the clay film correlates well with the ratio I_{pa}/I_{pc} that means that this is the predominant factor in the electroactivity of the corresponding organoclay modified electrodes.

Table 1

Half wave potentials ($E_{1/2}$), anodic peak current intensities (I_{pa}) and ratio of the anodic to cathodic peak current (I_{pa}/I_{pc}), obtained in 10^{-1} M Na_2SO_4 using CTA^+-ME, CTA^+-AME4 CTA^+-PME and CTA^+-PAME4 as working electrodes, after soaking for 2 hours in a 10^{-4}M $[Fe(CN)_6]^{4-}$aqueous solution.

Electrode	**I_{pa}(μA)**	**$E_{1/2}$ (mV/MSE)**	**$I_{p\alpha}$ /I_{pc}**
CTA^+-ME	17	-160	1,10
CTA^+-AME	19,4	-127	1,21
CTA^+-PME	1,85	-190	1,16
CTA^+-PAME	2,70	-200	1,69

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