Apparent Biphoresis in a Quartz Microbalance Study of the Electrodeposition of Phyllosilicate Sols

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In the electrodeposition of clay particles onto an electrode attached to a quartz microbalance crystal, which monitors the mass deposited, the occurrence of deposition when the electrode is cathodic or anodic indicates that the net-negative particles may also become attached by means of their positively charged edges.

The unique charge distribution on the platelets comprising clay colloids prompts continuing physicochemical interest. Structural and substitutional histories[1] leave a net-negative charge on the large basal faces of the platelets. By contrast, the sign and density of the charge at the edges of the platelets is pH dependent, positive edges being found in acidic media. This anisotropic charge distribution was inferred from an electron micrograph of a mixture of gold and kaolinite sols, the negative gold particles adhering exclusively to the positive edges of the kaolinite particles. Montmorillonite and bentonite show a similar charge anisotropy.[1,2] Clay particles may thus be electrodeposited onto anodes.[3]

In preliminary DC electrodeposition experiments with 2 × 2 cm^2 copper electrodes, deposits were observed to form on the cathode. Detailed studies were performed on a cell comprising a barely turbid sol,† a 5 mm Pt wire as a counter electrode and a gold-plated piezoelectric quartz crystal vertically beneath it, at a distance 2 cm away. The latter electrode served as a 'microbalance' monitoring the amount deposited, since its oscillation frequency depends linearly on the attached mass.[4] As thin films are electrodeposited onto the QCM working electrode, the oscillation frequency decreases. The value recorded is the difference in frequency between the working crystal and a frequency-invariant (10 MHz) reference crystal. Deposition was again observed with the working electrode anodic or cathodic. Experiments were conducted under DC and low-frequency AC fields at 20 °C.

Bentonite deposition, under a positive DC potential, shows a sharp initial increase followed by a monotonic rise in electrodeposited mass on the microbalance [Fig. 1(*a*) (*i*)]. As the clay platelet faces are negatively charged, this implies a continuous face-upon-face multilayer construction. In contrast, the deposited mass from the same clay colloid, now under a negative potential, rapidly levels off, as if in a monolayer fashion [Fig. 1(*a*) (*ii*)]. This can be understood if the (positive) platelet edges stand at right angles to the cathode surface in a nearly close-packed array, which would be limited in number by the face-to-face packing of this single-edge attachment. If the usual[5] aspect ratio 1 : 10 of such platelets is assumed,‡ together with the density of the

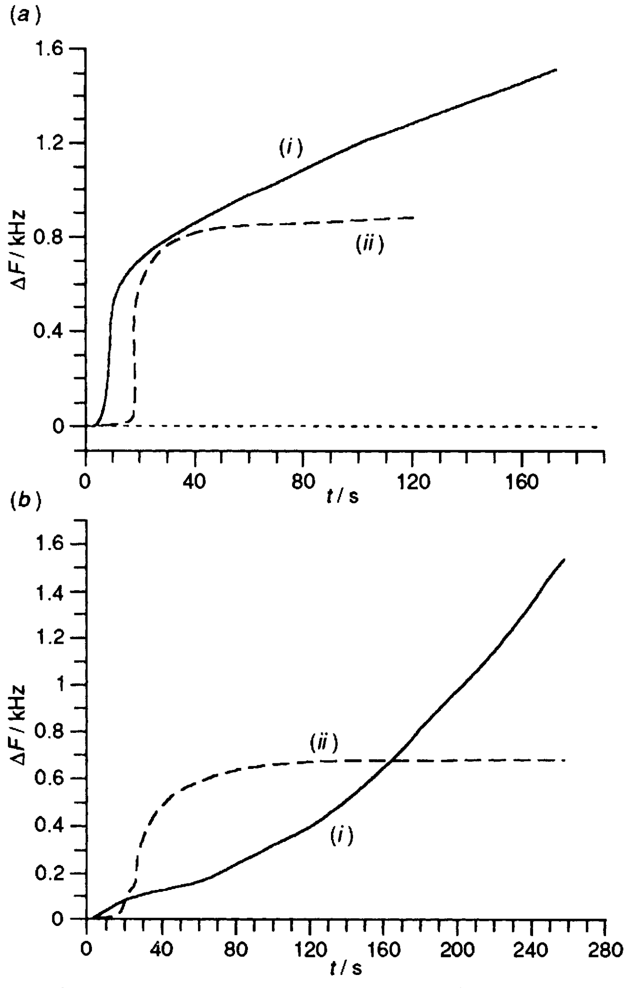

Fig. 1 Chronogravimetric trace for deposition of (*a*) bentonite and (*b*) montmorillonite under a DC field: (*i*) particle deposition on an anode; (*ii*) particle deposition on a cathode. Frequency difference ΔF is proportional to the mass deposited.[4]

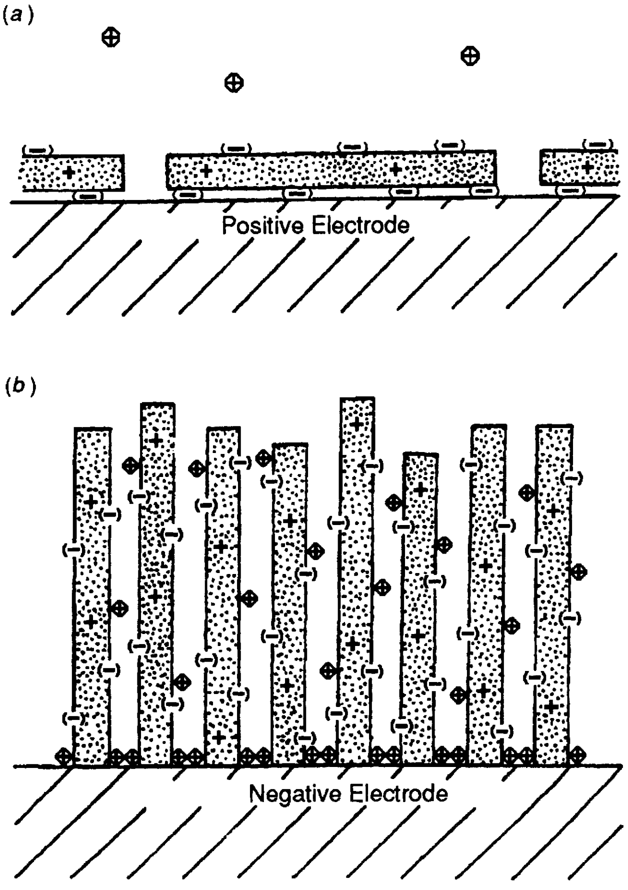

Fig. 2 Schematic representation of (*a*) face-wise deposition on a positive substrate, (*b*) the edge-on stance of platelets on a negative substrate, separated by cations drawn to the electrode from the face double layers

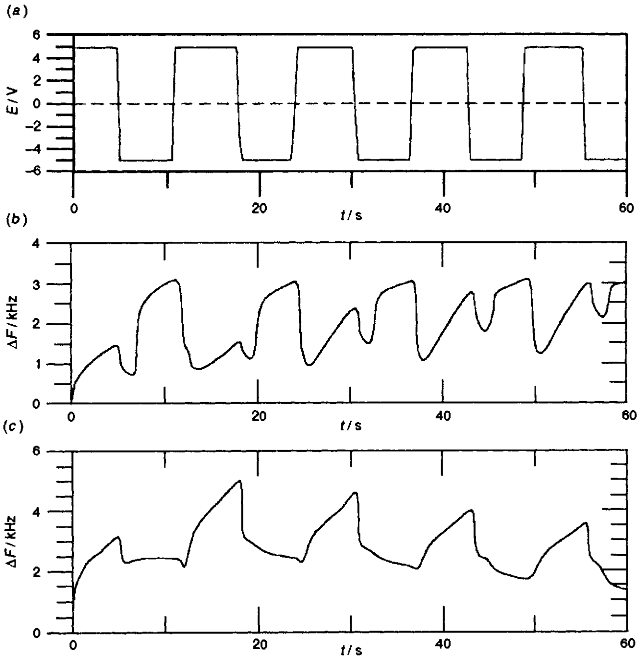

Fig. 3 Chronogravimetric traces for (*b*) bentonite and (*c*) montmorillonite depositing under a low frequency pulsed square wave (*a*). For (*b*) the correlation of particle adherence to, or loss from, the electrode with the phase of the applied field is apparent, while for (*c*) deposition occurs only on the positive phases, with incipient loss during the negative phases in later cycles.

electrodeposited material (when detached and dried, obtained as 1.8 ± 0.1 g cm^{-3} *cf.* 2.8 g cm^{-3} of consolidated material[5]), the inter-platelet spacing is obtained as 1.9 nm *cf.* a scanning electron micrograph-derived value of 1.14 nm in the parent clay. The wider spacing in the edge-attached deposit could result from the insertion of extra countercations between platelets standing normal to the surface, but uncertainty in the aspect ratio could credibly decrease the former figure by as much as one third.

Since bentonite comprises a mixture of montmorillonite and beidellite, montmorillonite alone was tested lest the observations arose from some sorting effect; the same general DC deposition behaviour was observed [Fig. 1(*b*), (*i*), (*ii*)]. The attachment of clay particles to an anode or cathode is depicted schematically in Fig. 2.

Chronogravimetric results were also obtained for the deposition of bentonite [Fig. 3(*b*)] and montmorillonite [Fig. 3(*c*)] under a low frequency (0.05 Hz) pulsed potential. For bentonite, deposition occurs when the electrode is made positive *or* negative, with some small loss from the electrode surface on change of polarity. In contrast to the DC measurements, deposition of montmorillonite under low frequency pulses occurs only on the positive steps. During the negative phases the mass, initially constant, in later cycles showed increasing loss. This is attributable to a difficulty (not experienced in bentonite)[§] in reversal of the facewise deposition of montmorillonite particles, there being insufficient time for edge attachment to ensue.

It is remarkable that overall-negative particles remain adherent on an electrode whose potential is switched from positive to negative. The diffusion of discs, and hence migration in an electric field, proceeds more readily edge-on than face-on due to the different diffusion coefficients[6,7] for the two orientations. Thus, discs deposited face-on to a (positive) electrode will, during the deposition, have undergone a rotary motion, aided by repulsion of the approaching positive edges. At the onset of the negative-electrode phase, this rotation will be reversed, allowing attraction of the edge by, then its attachment to, the electrode.

These electrodeposition experiments clearly demonstrate the utility of the quartz crystal microbalance in colloid electrodeposition studies and also show that clay colloid platelets, although bearing an overall-negative charge, can, under favourable solution conditions, attach themselves to an anode or a cathode.

A full account has been completed.[8]

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Footnotes

[†] *Clay origins*. BDH nominally sodium-form Wyoming-type bentonite from Black Hills, S. Dakota. Analysis, mass %: SiO_2, 57.5; Al_2O_3, 17.6; Fe_2O_3, 3.4; Na_2O, 3.8; MgO, 1.7; CaO, 1.0; CO_2, 1.0; H_2O, 10.0; other each <0.5. Sodium montmorillonite from English China Clays Intnl., St Austell. Analysis, mass %: SiO_2, 66.5; Al_2O_3, 17.3; Fe_2O_3, 3.4; Na_2O, 2.5; MgO, 2.0; CaO, 1.7; others <1.

Treatment: thrice soaked for 24 h in 0.1 mol dm^{-3} NaCl (centrifugal separation), solid washed in doubly deionised H_2O, centrifuged (8000 rpm, 50 kHz). Solid (5 g) + H_2O (250 cm^3) ground in Silverson high-shear mixer; liquid centrifuged off (30 kHz, 30 min) then diluted threefold gave slightly turbid stable suspensions of pH 5.5.

[‡] High shear grinding during preparation gives lower aspect ratios than the 1 : 100 sometimes encountered.

[§] H_2O adsorption only expands the montmorillonite *c* axis but ". . . bentonite . . . takes up water . . . multilaterally . . . dispersing the particles to form a gel."[9]

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