

## ELECTRODES MODIFIED WITH SYNTHETIC CLAY MINERALS: ELECTROCHEMISTRY OF COBALT SMECTITES

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**Abstract**—Hydrothermal treatment of a mixture of silicic acid, cobalt chloride, sodium dithionite and sodium hydroxide at 250 °C under 500 psi of argon produced a pink solid. X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction data showed the product to be a well-crystallized smectite. SEM/EDX analysis gave a unit cell formula of  $[(\text{Si}_{8.05})(\text{Co}_{5.58})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.66}$ . Heating the same mixture at 150 °C without argon gave a less well ordered smectite of composition  $[(\text{Si}_{7.93})(\text{Co}_{5.92})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.42}$ . Two peaks were observed in the cyclic voltammograms of electrodes modified with films of these two clays recorded for the blank electrolytes in the absence of any adsorbed electroactive species. The first peak was attributed to the oxidation of a small fraction of the  $\text{Co}^{2+}$  sites within the clay lattices to  $\text{Co}^{3+}$ . The second peak was assigned to further oxidation of these  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ .

**Key Words**—Clay-modified Electrodes, Cobalt, Cyclic Voltammetry, Smectites, Synthetic Clay.

### INTRODUCTION

Clay-modified electrodes (CME) are prepared by depositing thin films of clay onto conductive substrates (Bard and Mallouk 1992; Fitch 1990). The aim is to use the chemical and physical properties of the clay to control the sensitivity or selectivity of the electrode toward solution species. However, natural clay minerals are not electronically conductive (Wang et al. 1989). Electron transport for CMEs depends upon a combination of diffusion of adsorbed electroactive species through the films, and electron hopping between the adsorbed species. This causes two problems. The first is low electroactive fractions. The low mobility of ions within clay films means that only a small fraction of them can reach the conductive substrate to participate during the electrochemical reaction (Villemure and Bard 1990; King et al. 1987). Second, the electron transfer processes in CMEs do not actually occur within the clay interlayer spaces. To participate in the electrochemical reaction the intercalated species must first diffuse out of the interlayer spaces (Shaw 1989). Thus, the opportunity to exploit the geometry of the gallery spaces is lost.

The electroactive fraction can be increased by using smaller more mobile electroactive species. Kaviratna and Pinnavaia (1992) reported that up to 80% of the  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  adsorbed into CMEs could be reduced electrochemically. The efficiency of the diffusion of ions in clay films can also be improved by swelling of the clay into dilute electrolytes prior to the measurements to make the films more porous (Fitch and Lee 1993). However, to have net electron transfer occur deep within the clay interlayer spaces requires an alternative charge transport mechanism. One possibility would be to make use of electrochemically active transition metal centers within the clay lattice as ac-

ceptor/donor sites to relay electrons between ions within the interlayer spaces and the conductive substrate.

Iron sites within the smectite lattices have long been implicated in charge transport in CMEs. Oyama and Anson (1986) reported that structural Fe sites within montmorillonite could mediate the reduction of  $\text{H}_2\text{O}_2$ . Electroactive Fe sites within clay films have been used as part of the design of a glucose sensor (Ohsaka et al. 1990). Electron transfer from  $\text{Fe}^{2+}$  has been proposed to account for the anomalously larger first anodic wave of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (Rudzinski and Bard 1986) and  $[\text{Fe}(\text{bpy})_3]^{2+}$  (Villemure and Bard 1990) adsorbed into CMEs. The initial anodic to cathodic current ratio found for  $[\text{Fe}(\text{bpy})_3]^{2+}$  for CMEs increased when the number of  $\text{Fe}^{2+}$  sites in smectites was increased by partial reduction of the clay's structural  $\text{Fe}^{3+}$  (Xiang and Villemure 1992). Recently we have shown that redox active iron sites within a synthetic smectite could relay electrons between  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  and  $[\text{Fe}(\text{bpy})_3]^{2+}$  ions coadsorbed into CMEs (Xiang and Villemure 1995).

The involvement of redox active transition metal sites in the electrochemistry of electrodes modified with other nonconductive solids has also been reported. Castro-Martin et al. (1993, 1994) described redox active  $\text{Ti}^{4+}$  sites in zeolite-modified electrodes. Electron transfer between adsorbed  $[\text{Fe}(\text{CN})_6]^{4-}$  or  $[\text{Mo}(\text{CN})_8]^{4-}$  ions and redox active Ni sites in an electrode modified with a Ni-Al layered double hydroxide resulted in 4 to 6 fold increase of the electroactive fractions (Qiu and Villemure 1995).

Natural smectites do not normally contain large amounts of transition metals other than Fe (Newman 1987). Therefore, we undertook an investigation of electrode modification with synthetic smectites. Procedures for the preparation of smectites containing

most of the first row transition metals are available from the literature (Güven 1988). We report the preparation of two  $\text{Co}^{2+}$  smectites. Peaks are observed in the cyclic voltammograms of CMEs prepared with these 2 clays. They are attributed to the electrochemical activity of  $\text{Co}^{2+}$  centers within the clays.

## EXPERIMENTAL

### Preparation of the Cobalt Clays

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was obtained from Fisher Scientific (Fair Lawn, NJ). All other chemicals were obtained from Aldrich (Milwaukee, WI) and used without further purification.

The procedure used to prepare the Co clays was adapted from 2 published procedures. The reaction mixtures were prepared as described by Mizutani et al. (1991) for the synthesis of Fe smectites. Briefly,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1.61 g) was dissolved in 200 ml of 45 mM silicic acid at pH 3 ( $\text{Co}/\text{Si} = 0.75$ ). 2 g  $\text{Na}_2\text{S}_2\text{O}_4$  was added to prevent Co oxidation. 2 M NaOH (16.7 ml) was added dropwise under  $\text{N}_2$  to this pink suspension ( $\text{Co}/\text{OH}^- = 0.20$ ). The dark blue mixture produced was stirred in a tightly closed container at room temperature for 2 d, during which the color first turned to brown and then slowly returned to pink. If  $\text{Na}_2\text{S}_2\text{O}_4$  was omitted, the mixture turned dark brown, and the product of the hydrothermal treatment was a dark brown powder.

Hydrothermal treatments were done in a PPI locking autoclave. For the first smectite sample (Co-1), the autoclave was charged with 500 psi of argon, heated at 250 °C for 15 h with mechanical shaking, and allowed to cool for 6 h. These conditions were similar to those employed by Bruce et al. (1986) for the preparation of an NaCo-smectite. The second sample (Co-2) was obtained by heating the mixture at 150 °C for 50 h without argon. These conditions were used by Mizutani et al. (1991) to prepare 2:1 Fe clays.

The products were washed with distilled water, stirred in 1 M NaCl solution overnight to ensure complete conversion to the Na homoionic forms, washed again with distilled water and dialysed through a Spectra/por 3 membrane until negative Cl tests were obtained. The sized fractions were separated by centrifugation (Jackson 1949) and freeze-dried.

### Characterization of the Clays

The XRD data were obtained from a Philips X-ray diffractometer equipped with a graphite monochromator and a vertical goniometer, using  $\text{CuK}_\alpha$  radiation.

The TEM were recorded on a Philips 400T Transmission Electron Microscope operated at 120 KV. Bright-field images were recorded onto Kodak EM film ( $3.25 \times 4.25$  in.). Electron diffraction patterns were recorded on the same film at a camera length of 800 nm. Clay samples were embedded into LR White

(Hard formula) in gelatin capsules that were filled and capped. The resin was polymerized in an oven at 60 °C for 2 to 3 d. Sections (60–120 nm thickness) were cut with a diamond knife and collected onto carbon formvar-coated copper grids (Malla et al. 1993).

The elemental analyses of the clays were done by SEM/EDX on a JEOL JSM-6400 Scanning Electron Microscope equipped with a LINK EXL EDX analyzer. Samples were evaporated films of the clays on graphite supports.

The oxidation state of Co within one of the clays (Co-2) was determined by spectrophotometric analysis. Briefly, 0.146 g of Co-2 was dissolved in 12 ml of 1.8 M  $\text{H}_2\text{SO}_4$  and 2 ml of 49% HF in a boiling water bath for 30 min. 20 ml 2.5%  $\text{H}_3\text{BO}_3$  was added (Stucki 1981). The UV-Visible spectrum of the solution showed a peak at 509 nm, characteristic of  $\text{Co}^{2+}$ . No peak at 605 nm was found, showing the absence of  $\text{Co}^{3+}$  (Davies and Watkins 1970).

The cation exchange capacities (CEC) were estimated by adding the clays to solutions of  $[\text{Ru}(\text{bpy})_3]^{2+}$  or methyl viologen ( $\text{MV}^{2+}$ ) and measuring the amounts of the cations adsorbed by UV-Visible spectroscopy. The UV-Visible spectra were recorded on a Hewlett-Packard model 8452A diode array spectrophotometer.

### Electrochemical Methods

The clay modified electrodes consisted of approximately 300 nm thick clay films deposited onto 1  $\text{cm}^2$  pieces of In-doped,  $\text{SnO}_2$  coated glass. They were prepared by spin coating drops of 10 g/l clay gels at 3000  $\text{rev min}^{-1}$  as described previously (Villemure and Bard 1990). The electrochemical measurements were made with a Princeton Applied Research PARC model 270-1 electrochemical analysis system utilizing an undivided three-electrode cell. The counter-electrode was a Pt screen and the reference was a saturated calomel electrode (SCE). The electrolyte solutions were degassed by bubbling with  $\text{N}_2$  prior to the measurements.

## RESULTS AND DISCUSSION

### Characterization of the Synthetic Clays

The first product (Co-1) was a pink flocculent solid easily dispersed into water. Its cation exchange capacity (CEC) estimated from the amounts of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{MV}^{2+}$  adsorbed by the solid was 0.64 meq/g, somewhat smaller than what is commonly found for natural smectites (Jaynes et al. 1986). Results of the SEM/EDX elemental analysis of the clay gave a calculated unit cell formula of  $[(\text{Si}_{8.05})(\text{Co}_{5.59})\text{O}_{20}(\text{OH})_4] \text{Na}_{0.66}$ . (Based upon  $\text{O}_{20}(\text{OH})_4$  expected for 2:1 layer silicates (Newman 1987). Co and Si contents from SEM/EDX, Na content from the CEC) in good agreement with what is expected for trioctahedral smectites (Newman 1987).

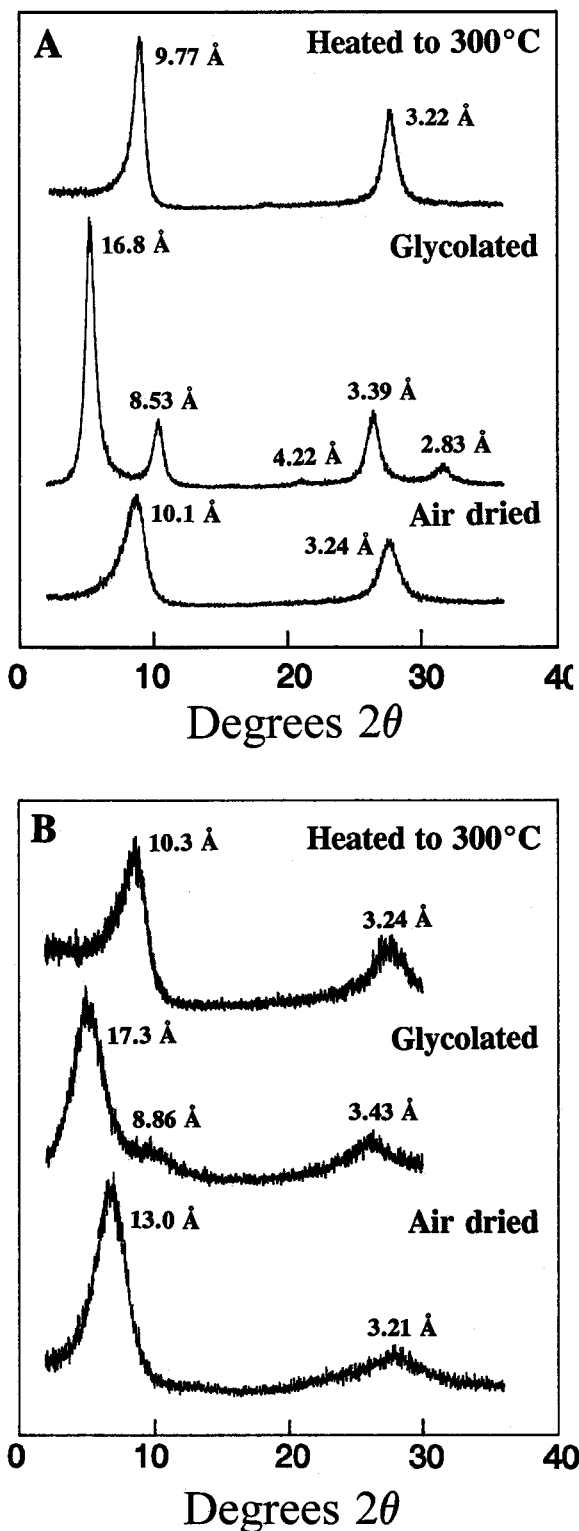


Figure 1. XRD patterns of oriented films of the synthetic Co-smectites: A) Co-1 (<0.2 μm fraction); and B) Co-2 (<2.0 μm fraction).

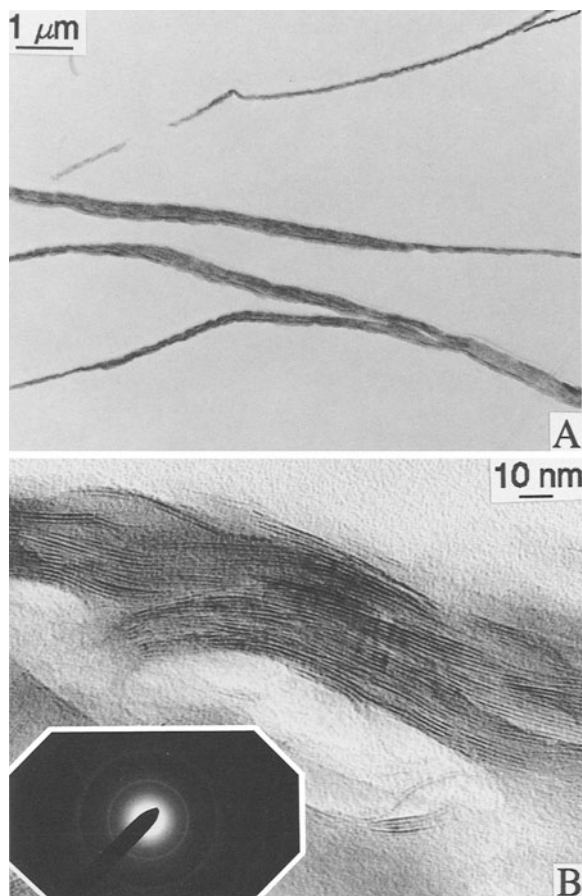


Figure 2. TEMs of the first cobalt smectite, Co-1.

Bruce et al. (1986) have previously prepared a NaCo-smectite by hydrothermal treatment of a slurry of colloidal silica,  $\text{Co}(\text{NO}_3)_2$  and NaOH at 250 °C under 3.4 MPa of  $\text{H}_2$ . Their product, described as a bright blue solid, contained more Co and slightly less Si than the clay made here. Its formal layer charge  $\sim 0.2$  per  $\text{O}_{20}(\text{OH})_4$  was also much lower than that of our clay.

Figure 1A shows the XRD patterns of an oriented film of the solid. The air-dried film had a basal spacing of 10.1 Å. The basal spacing of 16.8 Å obtained when the film was exposed to glycol, which shifted down to 9.8 Å when the film was heated to 300 °C, are characteristic of swelling smectite clays (Brindley and Brown 1980). Basal spacings of 13 Å were obtained for air-dried films of the  $\text{Ca}^{2+}$  exchanged form of the clay. A film exchanged with methylviologen ( $\text{MV}^{2+}$ ) had (001) spacings of 12.5 Å, similar to what was found for natural smectites intercalated with this cation (Villemure et al. 1985).

Figure 2 shows transmission electron micrographs of the clay. There were no indications of more than one type of particle. The product consisted exclusively of long twisting ribbons (Figure 2A). At high magni-

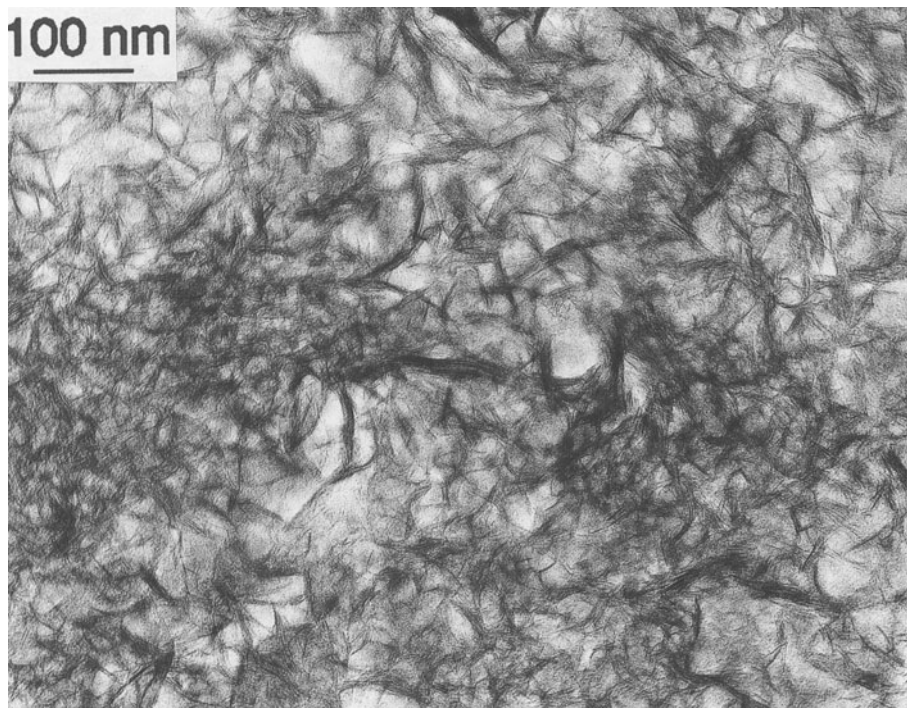


Figure 3. TEM of the second cobalt smectite, Co-2.

fication, the edges of the layers stacked “book like” are clearly seen (Figure 2B). The spacings between the layers were of the order of 12 Å. Electron diffraction from small area of the sample (Figure 2B, Inset) gave the ring pattern expected for a layer material. The positions of the strong reflections 4.74 Å, 2.71 Å, 1.57 Å and 1.37 Å agree well with those reported by Bruce et al. (1986). TEM/EDX analysis of the layers gave chemical compositions very similar to that obtained by SEM/EDX.

The UV-Visible spectrum of a suspension of the clay had a broad absorption band centered at 19,450  $\text{cm}^{-1}$ . The pink color is characteristic of octahedrally coordinated  $\text{Co}^{2+}$ . Absorption bands between 19,000 to 20,000  $\text{cm}^{-1}$  attributed to  ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$  transition of high-spin  $\text{Co}^{2+}$  in octahedral coordination are found for many Co-containing minerals (Faye and Nickel 1968; Rossman 1988). Bruce et al. (1986) attributed the blue color of their NaCo-smectites to tetrahedral  $\text{Co}^{2+}$  substitutions. Acid washing of their clay gave a pink solid with an adsorption maximum at 19,400  $\text{cm}^{-1}$ .

The IR spectrum showed O-H stretching of the structural OH bands at 3631  $\text{cm}^{-1}$  and 3510  $\text{cm}^{-1}$ , a broad band at 3418  $\text{cm}^{-1}$  attributed to interlayer  $\text{H}_2\text{O}$ , and a band at 668  $\text{cm}^{-1}$  assigned to a deformation mode of OH linked to 3 Co atoms (Bruce et al. 1986).

The second clay sample (Co-2) was similar in appearance to Co-1. Its calculated formula  $[(\text{Si}_{7.93})(\text{Co}_{5.92})$

$\text{O}_{20}(\text{OH})_4]\text{Na}_{0.42}$  showed that it contained slightly less Si but significantly more Co than Co-1. Its CEC of 0.39 meq/g was smaller than that of Co-1. Its XRD pattern (Figure 1B) showed a broad peak around 13 Å, that shifted to > 17 Å when the film was exposed to glycol, and down to 10 Å when the film was heated to 300 °C. Transmission electron microscopy showed smaller particles and less well-resolved clay fringes (Figure 3). Co-2 did not give an electron diffraction pattern. The sample appeared to be a much less well-crystallized smectite than Co-1.

#### Electrochemistry of the Synthetic Co-Smectites

The cyclic voltammogram of a CME prepared with the Na form of the first synthetic Co-smectite (Co-1), recorded in sodium acetate pH 4.7 buffer is shown in Figure 4A. A broad voltammetric wave centred around 0.95 V was observed to grow during the first few scans. A stable voltammogram was obtained after approximately 20 scans.

When the pH of the electrolyte was increased, this wave split into 2 waves with different pH dependencies (Figure 4B). The first wave (anodic peak  $\text{I}_a$  and the cathodic peak  $\text{I}_c$ ) shifted to lower potential by 110 mV per pH unit, compared to only 70 mV per pH unit for the second wave (peaks  $\text{II}_a$  and  $\text{II}_c$ ). However, the 2 waves were not independent. Peak  $\text{I}_c$  only appeared if the potential was scanned above the potential of peak  $\text{II}_a$ . No waves were found when a fresh electrode

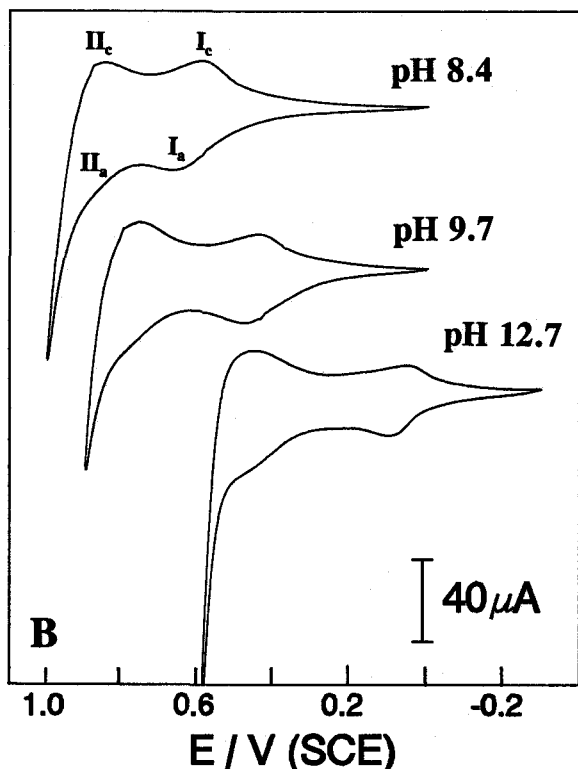
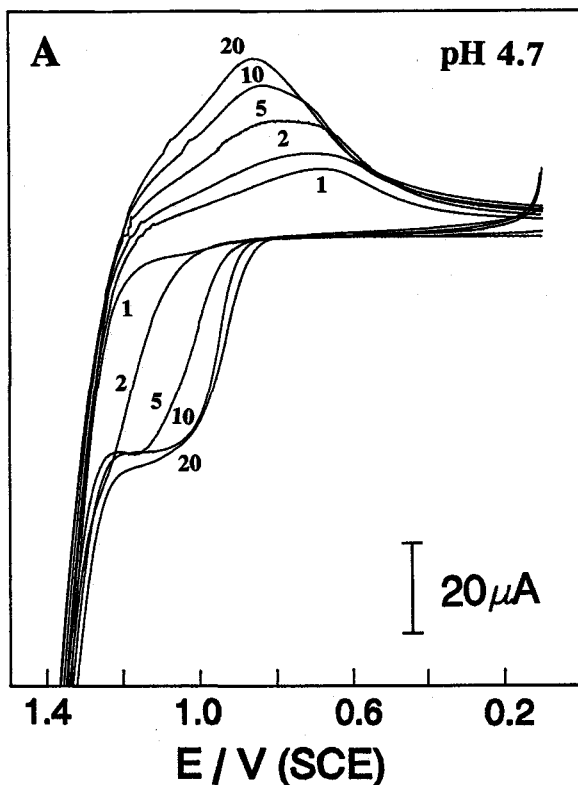


Figure 4. Cyclic voltammograms of electrodes modified with films of the synthetic smectite Co-1 (<0.2  $\mu\text{m}$  fraction):

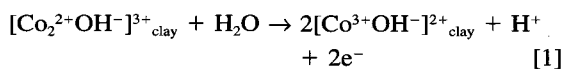
was scanned if the switching potential used was lower than the potential of peak  $\text{II}_a$ .

The cyclic voltammograms of electrodes modified with films of the second smectite (Co-2) were very similar to those of the Co-1 CMEs, except that Co-2 gave somewhat larger peak currents.

Since there were no adsorbed electroactive species present, we attribute these voltammetric waves to the oxidation of Co within the clay lattices. Cobalt was the only species present within the clays that had the potential to be redox active. The general shape of the voltammograms was also very similar to the voltammograms obtained when polycrystalline Co electrodes are cycled in basic solutions (Kessler et al. 1991).

We attribute peak  $\text{I}_a$  to the oxidation of some of the  $\text{Co}^{2+}$  sites within the clay lattices to  $\text{Co}^{3+}$ . The position of peak  $\text{I}_a$  and its dependence upon pH agree with those of the peaks assigned to the oxidation of  $\text{Co}^{2+}$  to various  $\text{Co}^{3+}$  phases ( $\text{Co}_3\text{O}_4$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{CoOOH}$ , and  $\text{CoHO}_2$ ) in the hydrous cobalt oxide films formed at the surface of Co electrodes during anodic passivation (Burke et al. 1982; Methios-Hukovic et al. 1991).

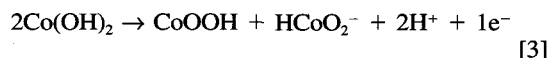
By analogy with the mechanism proposed for the oxidation of  $\text{Fe}^{2+}$  in natural smectites, hydration followed by rapid proton loss (Stucki and Lear 1990), the following reaction may be written:



However, the pH dependency of peak  $\text{I}_a$  was 110 mV per pH unit. This requires the loss of  $\sim 2 \text{H}^+$  per  $\text{e}^-$  transferred. Among reactions that would fulfill this condition are oxidation to a  $\text{CoO}_2^-$  phase (Milazzo and Caroli 1978),



or oxidation to an oxyhydroxide phase combined with the production of soluble  $\text{Co}^{2+}$  species,  $\text{HCoO}_2^-$  (Kessler et al. 1991).



Irrespective of the precise formulation of the oxidation reaction, only a tiny fraction of the  $\text{Co}^{2+}$  sites were actually oxidized during any given scan.

The second wave, peaks  $\text{II}_a$  and  $\text{II}_c$ , is assigned to further oxidation of  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$



There are many precedents from the literature for ox-

←

A) 1st to 20th scan in 0.05 M sodium acetate buffer pH 4.7; and B) For 0.05 M sodium borate buffer pH 8.4, 0.05 M sodium carbonate buffer pH 9.7 and 0.05 M NaOH pH 12.7 (20th scan, 50 mV/s). Subscript a refers to anodic peaks and subscript c refers to cathodic peaks.

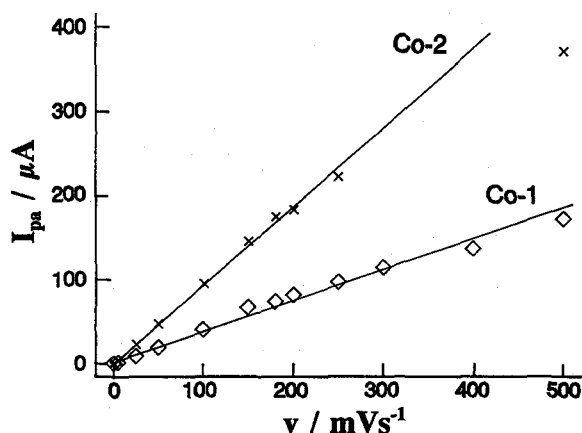


Figure 5. Peak current vs. scan speed for the first anodic peak ( $I_a$  in Figure 4B) in the voltammogram of cobalt CMEs (Recorded in 0.05 M sodium carbonate buffer pH 9.7).

oxidation of  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$  occurring just before or at the oxygen evolution limit (Burke et al. 1982; Kessler et al. 1991; Methios-Hukovic et al. 1991). The formation of  $\text{CoO}_2$  by oxidation of  $\text{Co}(\text{OH})_2$  films, or by anodic polarization of Co electrodes has been directly demonstrated by Mössbauer spectroscopy (Simmons et al. 1976, 1979).

Figure 5 shows plots of the peak current versus the scan speed for peak  $I_a$  of CMEs prepared with the two Co-smectites. For both cases, the peak current increased linearly with the scan speed up to at least 250 mV/s. This behavior is characteristic of thin layer non diffusing systems. From the slopes, the concentrations of electroactive centers within the films can be estimated as  $1.4 \times 10^{-5}$  for Co-1 and  $3.3 \times 10^{-5}$  mol/cm<sup>3</sup> for Co-2. This corresponds to the oxidation of only 0.13% for Co-1 and 0.30% for Co-2 of the  $\text{Co}^{2+}$  centers initially present within the CMEs.

One possible explanation for such low electroactive fractions is that only the  $\text{Co}^{2+}$  centers present in the first clay layer, the only one in direct contact with the conductive substrate, could be oxidized. Each CME consisted of approximately 300 clay layers (300 nm thick films). Therefore, the first layer contained ~0.33% of the  $\text{Co}^{2+}$  within the films, enough to account for the totality of the electroactivity. However, if this was the only explanation for the low electroactive fractions, the size of the voltammetric waves would be independent of the thickness of the clay films. This was not the case. The size of the waves increased when the film thickness was increased.

An alternative explanation is that activity was due only to  $\text{Co}^{2+}$  that was present at defect sites within the clay structures. For example, electroactivity could be restricted to the  $\text{Co}^{2+}$  present at the edges of the octahedral sheets. This argument would explain why the electroactive fraction was larger for Co-2. As we saw in the previous section, the principal difference be-

tween the two Co-smectites was that Co-2 was much less well-ordered than Co-1.

No waves attributed to direct electron transfer from clay structural sites have ever been reported for CME made from natural clays. The proposed redox activity of Fe within CME always involved an adsorbed electroactive species as charge mediator (Oyama and Anson 1986; Rudzinski and Bard 1986; Villemure and Bard 1990). The only previous example of voltammetric waves from CMEs containing no adsorbed electroactive species is for synthetic Fe smectites, for which peaks attributed to incompletely reversible oxidation of structural  $\text{Fe}^{2+}$  were observed during the first few scans (Xiang and Villemure 1995).

## CONCLUSIONS

Two clays containing Co as the only metallic element were prepared. The first was a well-crystallized smectite of composition  $[(\text{Si}_{8.05})(\text{Co}_{0.58})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.66}$ . The second was a less well-ordered smectite of composition  $[(\text{Si}_{7.93})(\text{Co}_{0.92})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.42}$ . Peaks were observed during the cyclic voltammograms of CMEs made with both clays, in the absence of any adsorbed electroactive species. They are attributed to the oxidation of small fractions (0.1 to 0.3%) of the  $\text{Co}^{2+}$  sites within the clay lattices to  $\text{Co}^{3+}$ , followed by further oxidation of the  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ . We are presently investigating electron transfer between these redox active Co sites and electroactive cations adsorbed within the CMEs.

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## REFERENCES

- Bard AJ, Mallouk TE. 1992. Electrodes modified with clays, zeolite and related microporous solids. *Technique of chemistry molecular design of electrode surfaces* 22:271–312.
- Brindley GW, Brown G. 1980. X-ray diffraction procedures for clay minerals identification. In: Brindley GW, Brown G, editors. *Crystal structures of clay minerals and their X-ray identification*. London: Mineralogical Society. p 305–360.
- Bruce LA, Sanders JV, Turney TW. 1986. Hydrothermal synthesis and characterization of cobalt clays. *Clays & Clay Miner* 34:25–36.
- Burke LD, Lyons ME, Murphy OJ. 1982. Formation of hydrous oxide films on cobalt under potential cycling conditions. *J Electroanal Chem* 132:247–261.

- Castro-Martins S de, Tuel A, Ben Taârit Y. 1994. Cyclic voltammetric characterization of titanium silicalite TS-1. *Zeolites* 14:130–136.
- Castro-Martins S de, Tuel A, Ben Taârit Y. 1993. Characterization of titanium silicalite using TS-1-modified carbon paste electrodes. *J Electroanal Chem* 350:15–28.
- Davies G, Watkins KO. 1970. The kinetic of some oxidation-reduction reactions involving cobalt(III) in aqueous perchloric acid. *J Phys Chem* 74:3388–3392.
- Faye GH, Nickel EH. 1968. The origin of pleochroism in erythrite. *Can Miner* 9:493–504.
- Fitch A. 1990. Clay-modified electrodes: A review. *Clays & Clay Miner* 38:391–400.
- Fitch A, Lee SA. 1993. Effect of clay charge on  $\text{Cr}(\text{bpy})_3^{3+}$  reaction mechanism at clay-modified electrodes. *J Electroanal Chem* 344:45–59.
- Guyen N. 1988. Smectites. In: Bailey SW, editor. *Hydrous phyllosilicates (exclusive of micas) reviews in mineralogy* Chelsea: Mineralogical Society of America 19:497–552.
- Jackson ML, Wittig LD, Pennington RP. 1949. Segregation procedure for the mineralogical analysis of soils. *Soil Sci Soc Am Proc* 14:77–81.
- Jaynes WF, Bigham JM. 1986. Multiple cation-exchange capacity measurements on standard clays using a commercial mechanical extractor. *Clays & Clay Miner* 34:93–98.
- Kaviratna P de S, Pinnavaia TJ. 1992. Electroactive  $\text{Ru}(\text{NH}_3)_6^{3+}$  gallery cations in clay-modified electrodes. *J Electroanal Chem* 332:135–145.
- Kessler T, Visintin A, Triaca WE, Arvia AJ, Gennero De Chialvo MR. 1991. Preparation and modification of hydrous thick cobalt oxide layers: Voltammetric characteristic of rough  $\text{Co}_3\text{O}_4$ -spinel-type electrodes. *J Appl Electrochem* 21:516–523.
- King RD, Nocera DG, Pinnavaia TJ. 1987. On the nature of electroactive sites in clay-modified electrodes. *J Electroanal Chem* 236:43–53.
- Malla PB, Robert M, Douglas LA, Tessier D, Komarneni S. 1993. Charge heterogeneity and nanostructure of 2:1 layer silicates by high-resolution transmission electron microscopy. *Clays & Clay Miner* 41:412–422.
- Methikos-Hukovic M, Stupnisek-Lisac E, Sokolean D. 1991. Surface properties of the system: hard metal/Co coating/electrolyte. *J Appl Electrochem* 21:619–624.
- Milazzo G, Caroli S. 1978. Tables of standard electrode potentials. New York: John Wiley & Sons, Ltd. p 336–343.
- Mizutani T, Fukushima Y, Okada A, Kamigaito O, Kobayashi T. 1991. Synthesis of 1:1 and 2:1 iron phyllosilicates and characterization of their iron state by Mössbauer spectroscopy. *Clays & Clay Miner* 39:381–386.
- Newman ACD, Brown G. 1987. The chemical constitution of clays. In: Newman ACD, editor. *Chemistry of clays and clay minerals*. New York: Mineralogical Society. p 1–129.
- Ohsaka T, Yamguchi Y, Oyama N. 1990. A new amperometric glucose sensor base on bilayer film coating of redox-active clay film and glucose oxidase enzyme film. *Bull Chem Soc Jpn* 63:2646–2652.
- Oyama N, Anson FC. 1986. Catalysis of the electroreduction of hydrogen peroxide by montmorillonite clay coatings on graphite electrodes. *J Electroanal Chem* 199:467–470.
- Qiu J, Villemure G. 1995. Anionic clay modified electrodes: electrochemical activity of nickel(II) sites in layered double hydroxide films. *J Electroanal Chem* 395:159–166.
- Rossman GR. 1988. Optical spectroscopy. In: Hawthorne FC, editor. *Spectroscopic methods in mineralogy and geology, Reviews in mineralogy* Chelsea: Mineralogical Society of America. 18:207–243.
- Rudzinski WE, Bard AJ. 1986. Clay modified electrodes part VI. Aluminum and silicon pillared clay modified electrodes. *J Electroanal Chem* 199:323–340.
- Shaw BR. 1989. Modification of solid electrodes in electroanalytical chemistry 1978–1988. In: Stock JT, Orna MV, editors. *Electrochemistry past and present, ACS Symposium Series 390*. Washington: American Chemical Society. p 318–338.
- Simmons GW, Kellerman E, Leidheiser H, Jr. 1976. In situ studies of the passivation and anodic oxidation of cobalt by emission Mössbauer spectroscopy. *J Electrochem Soc* 123:1276–1284.
- Simmons GW, Vértes A, Varsanyi ML, Leidheiser H, Jr. 1979. Emission Mössbauer studies of anodically formed  $\text{CoO}_2$ . *J Electrochem Soc* 126:187–189.
- Stucki JW. 1981. The quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline: II. A photochemical method. *Soil Sci Soc Am J* 45:638–640.
- Villemure G, Bard AJ. 1990. Clay modified electrodes part 9: Electrochemical studies of the electroactive fraction of adsorbed species in reduced-charge and preadsorbed clay films. *J Electroanal Chem* 282:107–121.
- Villemure G, Kodama H, Detellier C. 1985. Photoreduction of water by visible light in the presence of montmorillonite. *Can J Chem* 63:1139–1142.
- Xiang Y, Villemure G. 1995. Electrodes modified with synthetic clay minerals: Evidence of direct electron transfer from structural iron sites in the clay lattice. *J Electroanal Chem* 381:21–27.
- Xiang Y, Villemure G. 1992. Electron transport in clay-modified electrodes: study of electron transfer between electrochemically oxidized tris (2,2'-bipyridyl)iron cations and clay structural iron(II) sites. *Can J Chem* 70:1833–1837.
- Wang D, Yu W, Zhu B. 1989. A special solid electrolyte-montmorillonite. *Solid State Ionics* 34:219–223.

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