

Preliminary note

CLAY-MODIFIED ELECTRODES

PART II. ELECTROCATALYSIS AT BIS(2,2'-BIPYRIDYL)
(4,4'-DICARBOXY-2,2'-BIPYRIDYL)Ru(II)-DISPERSED RUTHENIUM
DIOXIDE-HECTORITE LAYERS

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We have recently reported the modification of electrode surfaces with a thin layer of a treated clay [a mixture of sodium-montmorillonite, colloidal platinum and polyvinyl alcohol (PVA)] and have described the electrochemical behavior of several substances incorporated into such films [1]. Apart from its usefulness as an ion-exchange mineral, the clay film also can function as a support material for highly dispersed metals and metal oxides. Thus, in addition to films cast from colloidal mixtures of clay/Pt/PVA, we have also been able to prepare stable films using clays treated with colloidal ruthenium dioxide (RuO_2). The function of the clay films is in this respect similar to that of polymers [2] which have been used as supports for platinum catalysts, either in the form of thin films [3-6] or as dispersed colloids [7]. In this preliminary account, we describe the voltammetric behavior of the zwitterionic species $\text{Ru}[\text{bpy}]_2 [\text{bpy}(\text{CO}_2)_2]$ (I) ($\text{bpy} = 2,2'$ -bipyridyl), at a sodium hectorite/ RuO_2 -modified tin oxide electrode*.

Experiments which have been carried out in this laboratory have indicated that uncharged solution species can readily diffuse through the clay films [9]. Moreover, platinum in the clay/platinum/PVA films is an active catalyst for reactions between solution species; for example, we have observed a large catalytic wave upon reduction of propyl viologen sulfonate (PVS) at these electrodes (presumably due to reduction of protons), although no such catalysis was evident for incorporated methyl viologen (MV^{2+}) [9]. We report here that the neutral Ru(II) complex, (I), shows catalytic activity in clay/ RuO_2 /PVA films. Note that recent reports have indicated that RuO_2 efficiently promotes the reduction of $\text{Ru}(\text{bpy})_3^{3+}$, in aqueous solution with concomitant formation of oxygen [10, 11].

*Na-hectorite is a 2 : 1 expandable layer lattice mineral with a cation exchange capacity of 100 meq/100 g. Colloidal RuO_2 was prepared from RuCl_3 by a modification of the literature procedure of ref. 8.

Films were cast on tin oxide electrodes from a colloidal dispersion comprising 4 g/L sodium hectorite, 0.035 g/L RuO_2 , and 1 g/L PVA (polyvinyl alcohol).

In Fig. 1 are shown cyclic voltammograms (CV) of $\text{Ru}[\text{bpy}]_2[\text{bpy}-(\text{CO}_2)_2]$ (I) at (1) a bare SnO_2 electrode, (2) at an $\text{SnO}_2/\text{clay}/\text{PVA}$ or $\text{SnO}_2/\text{clay}/\text{Pt}/\text{PVA}$ electrode, and (3) at an $\text{SnO}_2/\text{clay}/\text{RuO}_2/\text{PVA}$ electrode. Curve 4 is the CV of $\text{SnO}_2/\text{clay}/\text{RuO}_2/\text{PVA}$ in pure supporting electrolyte. All traces were obtained in unbuffered $0.1\text{ M Na}_2\text{SO}_4$ adjusted to pH 7. The CV of (I) is virtually identical at a bare SnO_2 electrode and at a clay/Pt/PVA-coated electrode (curves 1 and 2). This suggests that (I) freely diffuses through the clay film ($D \cong 3 \times 10^{-6}\text{ cm}^2/\text{s}$) (as contrasted with $\text{Ru}(\text{bpy})_3^{2+}$, which shows a much smaller D -value [1, 9]). There is a dramatic change in the CV behavior of (I) when RuO_2 is incorporated into the clay matrix (compare curves 2 and 3); the reversible voltammogram of (I) is replaced by an S-shaped curve (5 mV/s), characteristic of a chemical reaction following the electron transfer step that regenerates the electroactive material (i.e., a catalytic or EC' mechanism)

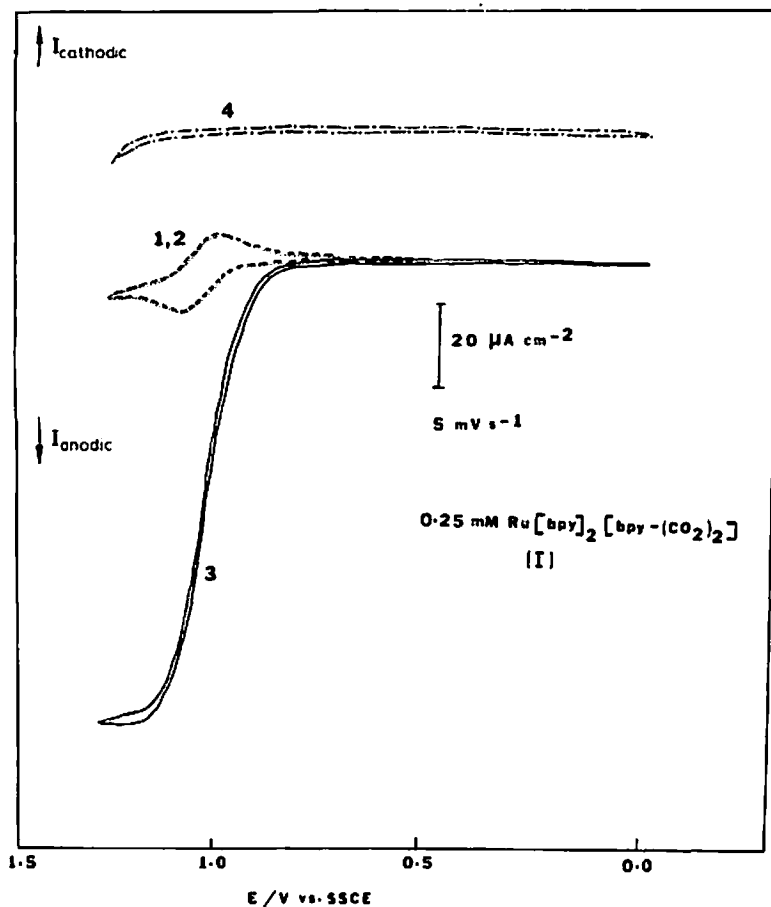


Fig. 1. Cyclic voltammograms of (I) (1) at a bare SnO_2 electrode (---), (2) at a sodium hectorite/PVA (or sodium hectorite/Pt/PVA)-coated SnO_2 electrode (....), and (3) at a sodium hectorite/ RuO_2 /PVA-coated SnO_2 electrode (—). (4) Cyclic voltammogram of a sodium hectorite/ RuO_2 /PVA-coated SnO_2 electrode in pure supporting electrolyte (-:-). The supporting electrolyte was $0.1\text{ M Na}_2\text{SO}_4$ (pH 7) in all experiments and the electrode area was $\sim 1.2\text{ cm}^2$. Sweep rate 5 mV/s .

[12–14]*. The effect of the follow-up reaction could be suppressed by increasing the sweep rate; at scan rates > 100 mV/s the voltammogram was essentially identical to those obtained in the absence of RuO_2 in the film. The voltammograms were also dependent on pH, with greater reversibility observed at lower pH values.

Although we have not yet carried out bulk electrolysis and examined the product(s) resulting from the reaction, we tentatively assign the follow-up chemical step to RuO_2 -mediated oxidation of water by the electrogenerated Ru(III) species with regeneration of the Ru(II) complex. Our conclusion is based on the observed pH-dependence of the reaction, the fact that bubbles are observed on the electrode when the reaction is carried out at pH 9.5 and the literature precedence for such a catalytic effect [10, 11]. Oxidation of the PVA is not involved, since similar behavior is found with $\text{SnO}_2/\text{clay}/(\text{I})$, RuO_2 films not containing PVA, although such films are less stable. Further work on the elucidation of this system is currently in progress.

ACKNOWLEDGEMENT

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*Note that no chemical step was seen for $\text{Ru}(\text{Bpy})_3^{2+}$ incorporated into the film. The voltammograms in this case were reversible, with $(i_p)_c/(i_p)_a \sim 1$.