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Short communication

CLAY MODIFIED ELECTRODES

PART VIII. ELECTROCHEMICAL BEHAVIOR AT MONTMORILLONITE AND POLYPYRROLE-MONTMORILLONITE FILMS ON PLATINUM AND GLASSY CARBON ELECTRODES

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INTRODUCTION

The electrochemistry of electrodes modified by coverage with either clay or organic polymer films has recently been investigated actively [1]. There has been a growing interest in the nature of various processes which govern charge transport at modified electrodes and also in the elucidation of the structure of the films. The electrochemical polymerization of pyrrole to prepare thin electronically conductive films has been reported extensively [2,3], mainly using acetonitrile (MeCN) as solvent. Recently, because of colloidal clays' appreciable surface area, intercalation properties, low cost, high stability and high cation exchange capacity, their use for electrode modification has become a very active research area [4]. An electrochemical method for producing flexible copolymer films from ionically conductive Nafion[™] perfluorosulfonic acid membranes (Du Pont) and electronically conductive polypyrrole was recently reported by our group [5a] and Penner and Martin [5b] and later by others [6]. These films have good electronic conductivity and high cation exchange capacity. The pursuit of systems with good conductivity and mechanical stability or showing a high capacitance has led us to investigate the possibility of making a biconductive film from clay and polypyrrole on the surface of platinum and glassy carbon electrodes. In this paper we describe the electrochemical behavior of these modified electrodes in the presence of several redox couples such as $\text{Fe}(\text{CN})_6^{3-4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{MV}^{2+/+}$ (where MV^{2+} is (*N,N'*-dimethyl-4,4'-bipyridinium)). We also report how the structure of the clay film is affected by treatment with MV^{2+} as studied by X-ray techniques.

EXPERIMENTAL

Potassium ferricyanide (Matheson, Coleman and Bell) and hexammineruthenium(III) chloride (99%, Aldrich) were reagent grade and used without further purification. *N,N'*-dimethyl-4,4'-bipyridinium dichloride (Sigma) was recrystallized from methanol + acetone. Pyrrole (Alfa) was purified by distillation from CaH_2 under N_2 . Tetra-*n*-butylammonium tetrafluoroborate (TBABF_4) (Southwestern Analytical Chemicals) was recrystallized from methanol. Distilled water for all experiments was from a Millipore water reagent system.

Instrumentation comprised a Princeton Applied Research (PAR) model 173 potentiostat-galvanostat, a model 175 Universal Programmer and model 179 Digital Coulometer. Cyclic voltammograms were recorded either on a Houston Instruments model 2000 X-Y recorder or on a Soltec VP-6432S X-Y₁-Y₂ recorder. The counterelectrode was a 2 cm² Pt gauze inserted directly into the solution. All solutions were deoxygenated for at least 30 min with purified N_2 and kept under N_2 throughout the experiments. A silver wire quasi-reference electrode and a SCE reference electrode were used in non-aqueous and aqueous solutions, respectively. The electrode areas were 0.07 cm² (glassy carbon), 0.018 cm² and 0.031 cm² (Pt). The clay colloid used in this work was the acid form of montmorillonite, H⁺-mont. The starting material was Ca-montmorillonite (STx-1, the Source Clay Minerals Depository, Univ. of Missouri, Columbia, MO) with a cation exchange capacity of 84 mmol univalent ion/100 g. An amount of 10 g of this clay was added to 200 ml 0.05 M HCl solution and stirred with a magnetic stirrer for 12 h. The suspension was centrifuged at 4000 rpm for 1 h. The supernatant was discarded and 200 ml of fresh 0.05 M HCl solution was added. This procedure was repeated six times. To remove the excess HCl, the same procedure was used with addition of distilled water instead of HCl. After four washings, the final opalescent supernatant was decanted and stored. This colloid (2.6 g/l) was stable against flocculation for several weeks. Platinum and glassy carbon electrodes were used as substrates. Three different types of modification were accomplished: (a) H⁺-montmorillonite films were prepared either by dropping a known volume (50 μl) of clay colloid (2.6 g/l) or by spin coating with the same solution as reported previously [4a]. The films were dried under ambient conditions, usually overnight (ca. 12 h). (b) Codeposited H⁺-mont./polypyrrole films were prepared by sweeping the bare electrodes in homogeneous aqueous solutions of H⁺-mont. (2.6 g/l) and pyrrole (50 mM), over the potential range -0.6 V to 1.0 V vs. SCE. The films were then thoroughly rinsed with distilled water. Homogeneous solutions of H⁺-mont. and pyrrole are very stable against flocculation for pyrrole concentrations up to ca. 30 mM. For pyrrole concentrations higher than 50 mM, sedimentation takes place. (c) Polypyrrole-clay films were prepared by sweeping the previously H⁺-mont. coated substrates in MeCN (spectrograde) solutions, 0.2 M TBABF_4 50 mM pyrrole, over the potential range -0.6 V to 1.0 V vs. Ag. It is assumed that 24 mC/cm² charge is equivalent to a 1 μm film [3]. The films were then thoroughly rinsed with MeCN.

RESULTS AND DISCUSSION

Type A electrodes (H^+ -mont. coated Pt and glassy carbon electrodes)

As expected, for anions, such as $Fe(CN)_6^{3-/4-}$, there is no evidence of a specific interaction between the clay films and the redox species, and only very small CV waves are observed [4d,f]. However, for the MV^{2+}/MV^+ couple, a sharp peak appeared at -0.6 V vs. SCE (in addition to the more typical broader peaks at -0.7 V) (Fig. 1). A study of this sharp peak at different scan rates, v , revealed that the peak current, i_p , was linearly proportional to v at v less than 50 mV/s. After cycling the electrodes in a solution containing 5 mM MV^{2+} and 0.5 M Na_2SO_4 and transferring the electrode to a solution containing supporting electrolyte alone, the small prepeak was not observed. This suggests that the species responsible for the prepeak is not strongly held within the electrode film. This prepeak might be related to the formation of a dimeric species which has been found in clay films by spectroelectrochemistry and electron spin resonance spectroscopy [4d]. For long term experiments (with more than 60 min cycling), a new wave appears at -0.35 V for reduction and -0.2 V vs. SCE for oxidation. Those observations appear specific to MV^{2+} , since similar behavior was not observed for other redox couples, such as $Ru(NH_3)_6^{2+/3+}$, which showed behavior typical of cations incorporated into clay films [4].

Type B electrodes (codeposited H^+ -mont.-polypyrrole films on Pt or on glassy carbon)

The cyclic voltammograms of these electrodes showed diffusion controlled waves for $Fe(CN)_6^{3-/4-}$ (i_p proportional to $v^{1/2}$). In the case of $Ru(NH_3)_6^{3+/2+}$ or

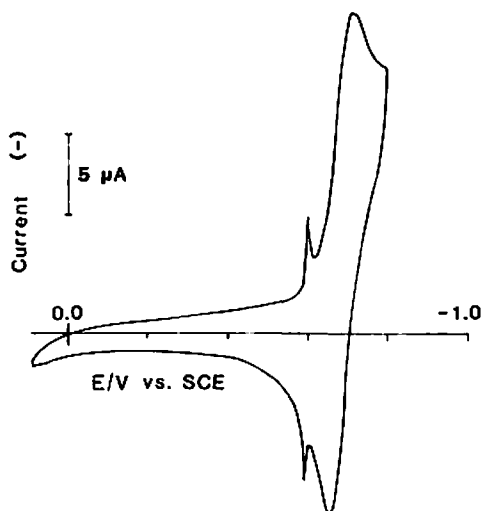


Fig. 1. Cyclic voltammogram on an H^+ -mont. coated Pt electrode in a 5 mM MV^{2+} + 0.05 M Na_2SO_4 solution. Scan rate: 50 mV/s. Electrode area: 0.018 cm 2 .

MV^{2+}/MV^+ , diffusion controlled waves were only observed at fast v (e.g., $v > 50$ mV/s). Thick films of this type could be peeled off of the substrate, and their electronic conductivity in the dry state was about two orders of magnitude less than pure polypyrrole films.

Type C electrodes (polypyrrole deposited on H^+ -mont. coated substrates)

These types of electrodes can be prepared to show different capacitance, depending on whether the clay coated electrodes have been treated with MV^{2+} before polypyrrole deposition. For a clay film that had not been treated with MV^{2+} the polypyrrole deposition rate was faster, as shown in Fig. 2, and this resulted in a film low capacitance ($\leq 10^{-3}$ F/cm²). This type of electrode showed diffusion con-

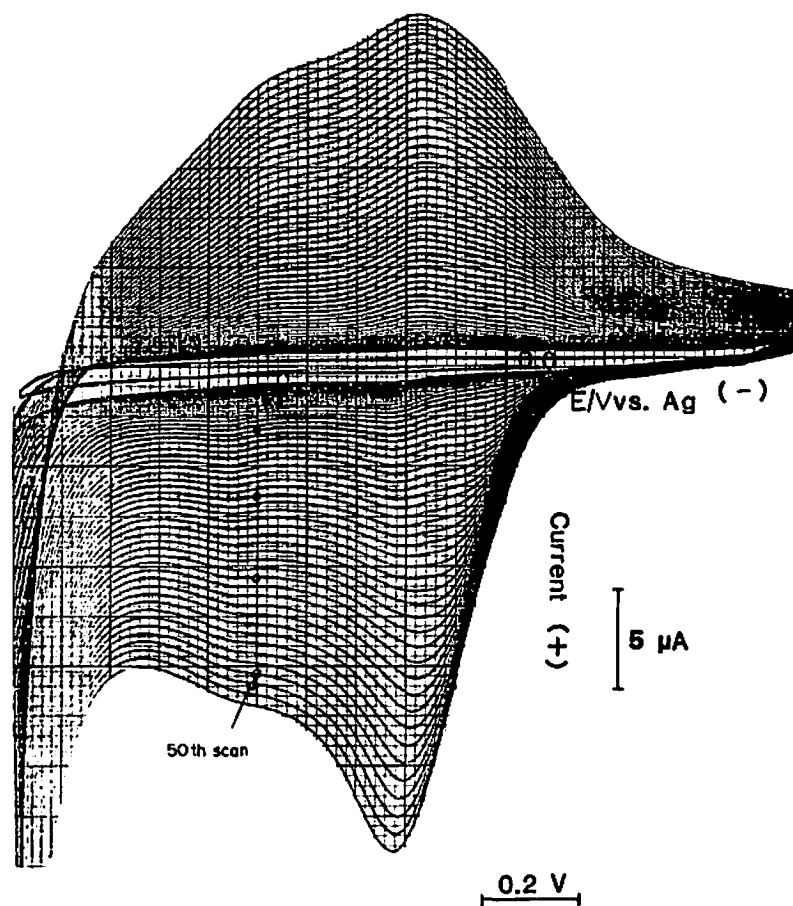


Fig. 2. Polypyrrole deposition onto an H^+ -mont. covered glassy carbon electrode. The clay film was not treated. Scan rate: 50 mV/s. Charge collected: 8.3 mC. Every 10th scan is marked with an open circle.

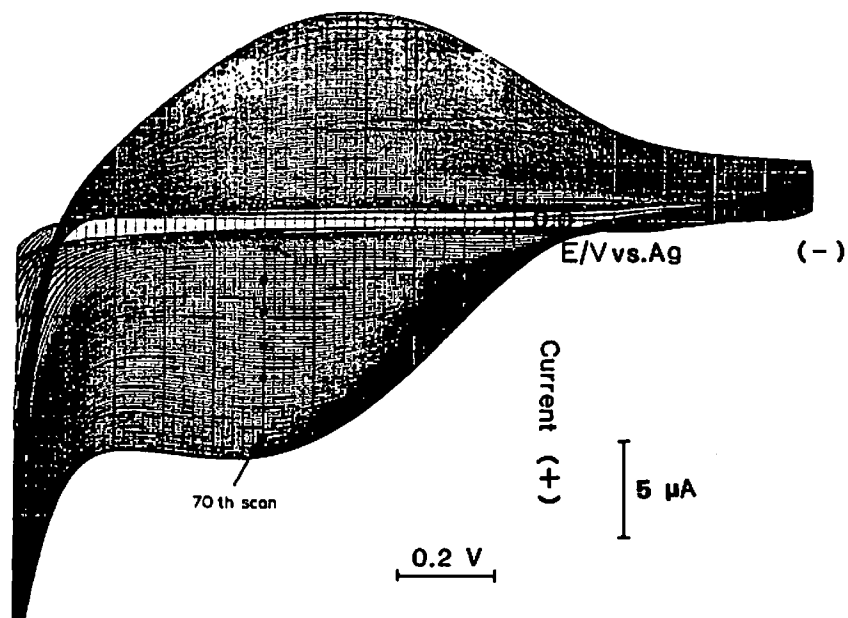


Fig. 3. Polypyrrole deposition onto an H⁺-mont. covered glassy carbon electrode. The clay modified electrode was previously treated with MV²⁺. Scan rate: 50 mV/s. Charge collected: 8.3 mC. Every 10th scan is marked with an open circle.

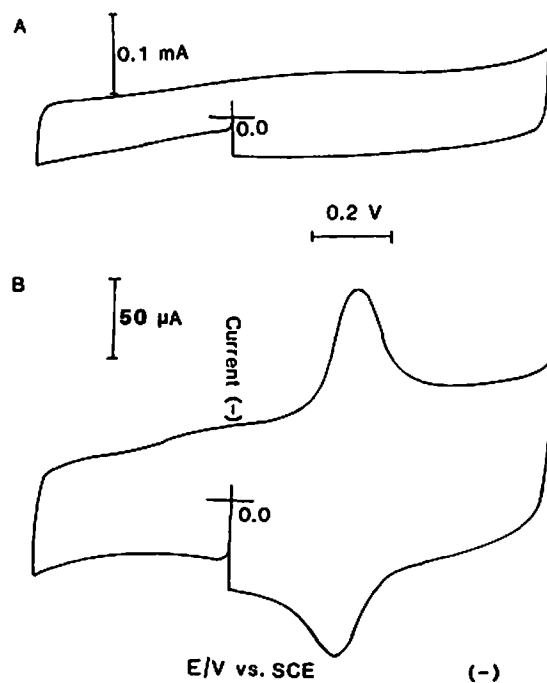


Fig. 4. Electrochemical behavior of a high capacitance film. (A) With supporting electrolyte (0.5 M Na₂SO₄). (B) With 0.004 M Ru(NH₃)₆^{3+/2+} + 0.5 M Na₂SO₄. Scan rate: 50 mV/s.

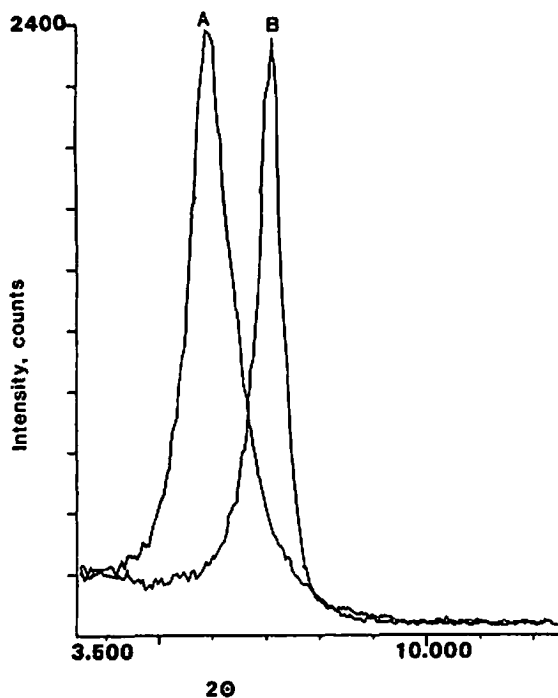


Fig. 5. X-ray patterns for clay films on SnO_2 substrates. H^+ -mont. before (A) and after (B) the treatment with MV^{2+} .

trolled CV for the redox reaction of $\text{Ru}(\text{NH}_3)_6^{3+}$ in a range of ν of 10–100 mV/s. If the film was treated with MV^{2+} before polypyrrole deposition, either by cycling between 0.0 and -0.8 V vs. SCE for 15 min or by soaking the electrodes in a 5 mM MV^{2+} solution for 30 min, the polypyrrole deposition proceeds at a lower steady rate (Fig. 3) and this affects the performance of these electrodes significantly (Fig. 4). Besides the high capacitance (of the order of 10^{-2} F/cm 2), they show thin layer electrochemical behavior at low ν for the redox reactions of MV^{2+} and $\text{Ru}(\text{NH}_3)_6^{3+}$. This electrochemical behavior indicates that the MV^{2+} treatment affects the structure of the clay films. This is supported by X-ray diffraction patterns as shown in Fig. 5, which demonstrate that after MV^{2+} treatment, a clay film shows greater organization than an untreated film; the diffraction peak is narrower and the lattice spacing changes from 1.487 nm to 1.241 nm. Such behavior is not seen following treatment of the clay films with other cations, such as $\text{Ru}(\text{NH}_3)_6^{3+}$, pointing to the uniqueness of the MV^{2+} -clay interaction [4d].

CONCLUSIONS

Polypyrrole-clay coatings can be prepared on various substrates (Pt, GC) or as free-standing films. The incorporation of polypyrrole into clay enhances the mecha-

nical stability of the films and produces electronically conductive films that show high capacitances. These high capacitances (ca. 10^{-2} F/cm² in the best films) are probably associated with a high surface area of the polymer [3c]. Such films might find application as electrodes or in electrochemical devices. The unique nature of the interaction of MV²⁺ with the montmorillonite films, previously studied by electrochemistry and electron spin resonance [4d], was confirmed here by X-ray diffraction measurements and electrochemical polypyrrole deposition experiments.

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