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Redox Behaviors of Viologen-Pendent Polypyrrole on Platinum Electrode. Ordered Electron Transfer between Electrode and Flavin Mononucleotide in Aqueous Media

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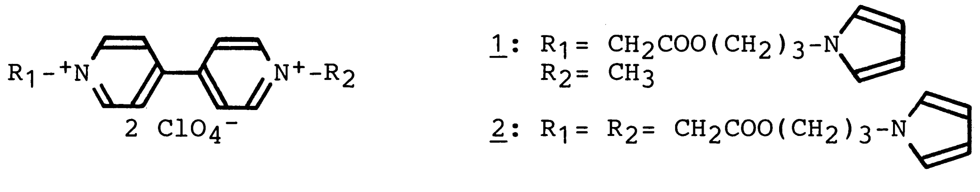
New Viologen linked pyrrole was polymerized by an electrochemical oxidation on platinum electrode to give a coated film, of which redox behaviors were investigated. Viologen linked pyrrole on one side of its N-alkyl substituents showed a reversible wave due to a redox reaction between viologen and viologen cation radical in aqueous media. An ordered electron-transfer was achieved by using the oriented viologen-pendent modified electrode in the cathodic redox reaction of flavin mononucleotide.

Electrochemical polymerizations have been paid much attentions for a development of new electro-active materials in the last decade.[1)] On the other hand, modifications on electrode surface have been carried out variedly in recent years.[2)] It is expected that a high content of functional group on the electrode surface and a high conductivity of coated film are achieved by an electrochemical polymerization of electro-active functional monomers. Some works along this line have been reported.[3)] Viologens (1,1'-dialkyl-4,4'-bipyridinium, V^{2+}) have been much noted as an electron-transfer mediator especially in conversion of light energy systems.[4)] There have been some reports[3a,3b,5)] on viologen modified electrodes which showed a reversible wave due to a redox reaction between V^{2+} and viologen cation radical ($V^{+\cdot}$).

In this paper, synthesis of new viologens linked pyrrole, electrochemical polymerization of the viologen linked pyrrole, and redox behaviors of the viologen polymer on platinum in aqueous media are investigated to achieve an ordered electron transfer among working electrode, conductive material, electron-transfer mediator, and biologically active material.

Two viologens linked pyrrole (1, 2) were prepared as follows; 3-aminopropanol was treated with 2,5-dimethoxytetrahydrofuran[3d)] to give

N-(3-hydroxypropyl)pyrrole which was esterified with bromoacetic acid to give (1-pyrrolyl)propyl α-bromoacetate. The bromoacetate was reacted with monomethylated 4,4'-bipyridine or 4,4'-bipyridine to give viologen linked pyrroles. The halogen anions of the viologens linked pyrrole were exchanged with ClO_4^- to give 1 and 2.



Electrochemical oxidation of 1 or 2 was carried out by a potential sweep method with a platinum disk electrode (Beckman) as a working electrode in CH_3CN-0.1 M tetrabutylammonium perchlorate. On a first potential sweep between 0 V and + 1.8 V (vs. SCE) at a rate of 100 mV s^{-1}, an anodic peak around + 1.2 V is observed clearly, but the peak current is decreased markedly by further sweeps. This phenomenon can be account for a rapid polymerization of pyrrole moiety in 1 on platinum surface, followed by suppression of electropolymerization due to aggregation of viologen moiety on the coated electrode. Cyclic voltammograms of these viologen-coated electrodes in CH_3CN did not show any redox waves in the cathodic region, in contrast to the result by Moutet et al.[3a,b] The different features might be due to the longer N-substituent of pyrrole.

A typical cyclic voltammogram in aqueous media of the polymer-coated electrode prepared by a potential sweep of 1 is shown in Fig. 1. The anodic and cathodic current peaks are separated by small ΔE_p (65 mV) and are symmetrically shaped irrespective of scan rates (0.01-0.2 V s^{-1}). Voltammetric peak currents of the redox wave are proportional to potential scan rates as the conventional polymer coating electrodes.[6] The half wave potential value ($E_{1/2}$) is - 0.45 V. It has been reported[7] that a redox potential around - 0.5 V is due to a redox reaction between V^{2+} and $V^{+\bullet}$. The results suggest the redox wave is due to a reversible one-electron-transfer reaction between viologen and electrode. However, an extra electropolymerization of 1 on platinum by several potential sweeps or by a controlled potential oxidation decreases the reversibility of the redox wave. In addition, the reversible redox wave was not observed in case of the viologen modified electrodes prepared by the electropolymerization of 2, viologen linked pyrrole moieties on both sides of N-substituents, which suggests that electrons do not transfer between electrode surface and viologen grouping selectively owing to the surrounding conductive polypyrrole grouping. From these results, an oriented structure of viologen-

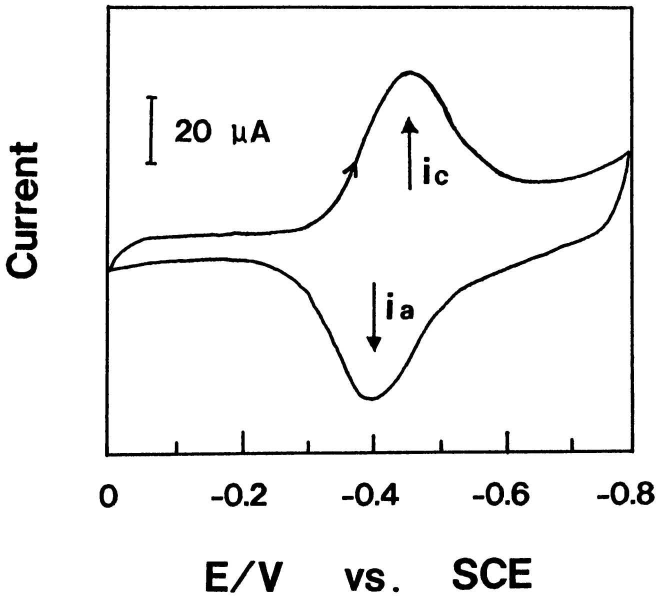


Fig. 1. Cyclic voltammogram of poly(1) coated film on Pt in H_2O-0.1 M $LiClO_4$.

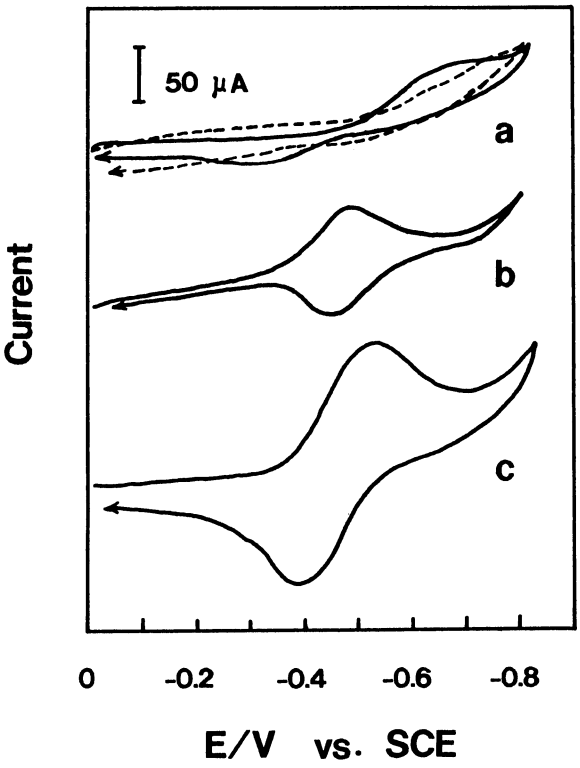
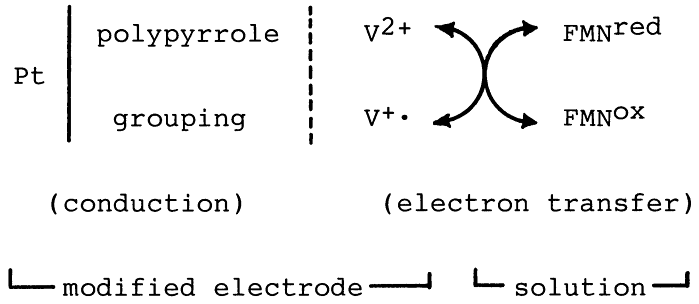


Fig. 2. A comparison of cyclic voltammograms in H_2O-pH 6.86 phosphate buffer-0.1 M Na_2SO_4; (a) in the presemce of FMN(2 mM) by unmodified Pt and by polypyrrole coated Pt(dotted line); (b) in the absence of FMN by poly(1)-coated Pt; (c) in the presence of FMN by poly(1)-coated Pt.

modified electrode is assumed. That is to say, the pyrrole moiety in 1 is electropolymerized selectively on platinum electrode surface, and viologen grouping is pendent from polypyrrol grouping. The decrease of a mobility of pendent viologen grouping and disordered viologen orientation on the electrode surface cause the irreversibility of the redox wave.

The viologen-modified electrode is compared with unmodified one by a cyclic voltammetry in the cathodic reaction of flavin mononucleotide (FMN)(Fig. 2). It has been reported[8)] that the redox potential of FMN is about - 0.2 V in a neutral aqueous condition. A broad unsymmetrical wave due to FMN redox reaction is observed, unable to determine the redox potential, when unmodified platinum electrode or a polypyrrole-coated platinum electrode is used as a working electrode. Contrarily, a symmetrical redox wave appears and a large current flows, when the poly(1)-coated electrode is used as a working electrode. The half wave potential value of the enhanced redox wave is - 0.46 V (vs. SCE), almost same to that of the poly(1)-coated electrode. The ΔEp value of the wave is about 90 mV and is almost invarient irrespective of scan rates (0.01-0.2 V s^{-1}). Peak currents are proportional to square root of potential scan rates. These results suggest that the cathodic redox reaction is a quasirversible electron transfer in solution system, and a catalytic electron-transfer to

FMN is occurred, mediated by the viologen grouping on platinum. An ordered electron-transfer among platinum, polypyrrole grouping, viologen grouping, and FMN can be demonstrated by using the oriented viologen-pendent modified electrode (Scheme 1).



Scheme 1. Ordered electron-transfer by viologen-modified electrode in cathodic reaction of FMN.

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