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Preparation and in Situ Reflection Spectra of Bilayer Electrodes with Polythiophene Outer Layers

Kenji MURAO* and Kazuhiro SUZUKI
Advanced Research Laboratory, Hitachi, Ltd.,
Kokubunji, Tokyo 185

Bilayer electrodes derived from 3-methylthiophene and bithiophene, Pt/poly[tris(4-vinyl-4'-methyl-2,2'-bipyridine)ruthenium(II) perchlorate]/polythiophene, have been prepared. Their in situ reflection spectra upon electrochemical potential sweeps suggest the transient occurrence of polarons in the doped polythiophenes.

It has been shown that the in situ optical spectra taken during the doping and undoping cycles of polypyrrole (poly(2,5-pyrrolylene)) and polythiophene (poly(2,5-thienylene)) provide important information on mid-gap states induced during the electrochemical processes.[1-3] However, such optical measurements have been confined to a configuration in which charge injections into conducting polymers are performed at metallic or conducting substrates. Therefore, it should be interesting to measure in situ optical spectra during charge injections into conducting polymers from discrete electronic levels of the adjacent, electrically insulating layer, since this configuration would allow electronic relaxations within the layer of conducting polymers to occur idependently of the Fermi level of the substrates. This paper describes the preparations and in situ reflection spectra of bilayer electrodes, Pt/poly[tris-(4-vinyl-4'-methyl-2,2'-bipyridine)ruthenium(II) perchlorate] (hereafter abbreviated as poly-1)/polythiophenes, which present direct evidence for the mediated redox reactions of polythiophenes via extrinsic layers. The polythiophenes are derived from 3-methylthiophene (MeT) and 2,2'-bithiophene (BT).

Platinum disks (4 mm diameter) and evaporated films of platinum (280 nm) on glass substrates were used as working substrates. Pt/poly-1 electrodes were prepared according to the reported method.[4] The electropolymerization of MeT was carried out galvanostatically at a current density of 275 μA cm^{-2} at a Pt/poly-1 electrode immersed in argon-purged anhydrous acetonitrile containing 120 mM MeT and 0.1 M TBAP (tetrabutylammonium perchlorate). The anodic charge passed during the deposition of poly-3-methylthiophene (PMeT) was typically 32.4 mC cm^{-2}. The potential applied to the working electrode reached a steady value of 1.17 V (hereafter, potentials are indicated vs. Ag/Ag^{+} [5]) within 10 s after the onset of anodization. This value is substantially larger than the II/III oxidation potential of poly-1 ($E^{0\prime}$= 0.875 V). This means that the electropolymerization of MeT occurs at the surface of the platinum substrate instead of mediated oxidation by poly-1. This is consistent with the cyclic voltammogram (CV) for the initial

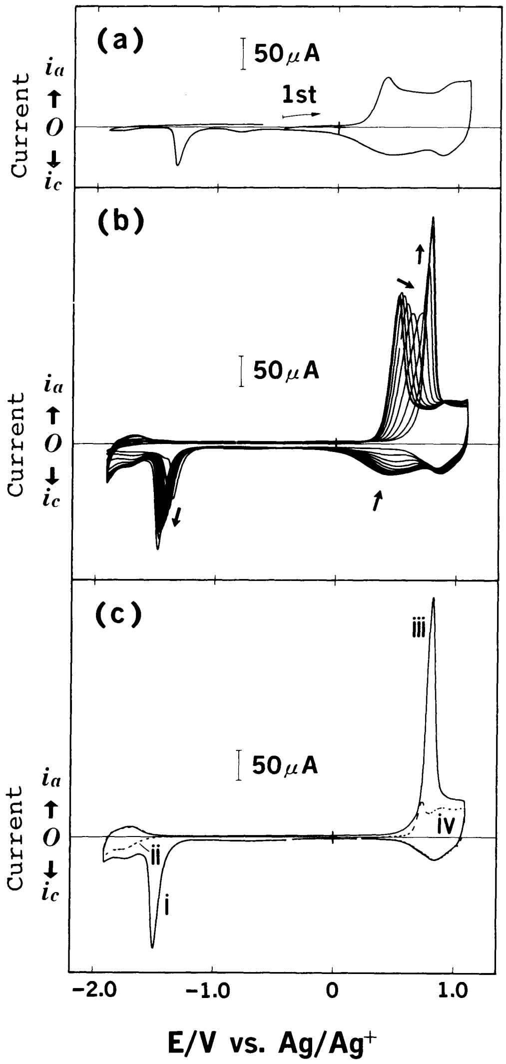

Fig. 1. Cyclic voltammograms for the poly-3-methylthiophene deposited Pt/poly-1 electrode. (a): 1st sweep, (b): subsequent 28 sweeps (recorded after every two sweeps), (c): the finally obtained waveform after 30 sweeps from (a). The arrows indicate the directions of the change. The potentials were swept in (c) as follows;

$$\begin{tikzcd}
 & -1.00 \arrow[d, shift left, "ii"] & +0.25 \arrow[d, shift left, "iv"] \\
-0.38 \arrow[r, "i"] & -1.90 \arrow[u, shift left] \arrow[r, "iii"] & +1.10 \arrow[u, shift left] \arrow[ll, bend left]
\end{tikzcd}$$

sweep of the electrode (Fig. 1(a)), where the essentially superimposed CV waves for PMeT and poly-1 are observed in the positive region of the potential. On the other hand, in the negative potential region, where PMeT is electrochemically inert, the 2+/1+ redox waves of the $Ru(bpy)_3$ moiety of poly-1 are totally absent except for a spiky current peak centered at -1.33 V, indicating that poly-3-methylthiophene present at the platinum electrode surface is blocking the reduction of the Ru(II) complex centers. Subsequent sweeps in TBAP/acetonitrile caused the changes of the CVs as shown in Fig. 1(b). Observed changes are as follows; 1) Anodic peak shifts of PMeT to the positive direction followed by peak growths as a prewave of the II/III wave for the $Ru(bpy)_3$ centers, 2) cathodic wave loss for PMeT, 3) growths of the spiky peak at -1.33 V with slight shifts towards the negative direction, 4) evolution of the 2+/1+ waves for $Ru(bpy)_3$ centers. In Fig. 1(c), the large spiky current peaks (i and iii) are observed only for virgin scans in negative and positive directions after allowing the spiky current peaks of the opposite signs, respectively. When potential sweeps are repeated in the same direction, the second sweeps produces small waves only (ii and iv), which reproduce the CV waves for Pt/poly-1 before PMeT is deposited, except for a residual small peak in iv. These observations in Fig. 1(c) mean that the oxidation and reduction of PMeT are mediated by poly-1, and are essentially consistent with the electrochemistry of bilayer electrodes.[4,6-8] The CV changes mentioned above [1)-4)] should be regarded as representing certain dynamic processes that cause phase separation of poly-1 and polythiophene which are initially intermingled, since the CV changes are essentially consistent with those observed when Pt/poly-1/polypyrrole bilayer electrodes[8] are prepared through phase separation of poly-1 and polypyrrole.[9]

The galvanostatic electropolymerization of BT at poly-1 occurred at 0.83 V which is slightly lower than the $E^{0\prime}$ value for II/III of poly-1. The first sweep of the PBT-as-deposited electrode also showed blocking of 2+/1+ waves of poly-1 by the surface PBT in the negative potential region, implying that BT is oxidized at the surface of the platinum substrate, and that the mediation of poly-1 on BT anodization is less likely. Subsequent sweeps induced similar CV changes as shown in Figs. 1(a)-(c), leading to the waveform of a typical bilayer electrochemistry. These results are important in that the bilayer electrodes of PMeT and PBT are obtained through similar processes to the case of polypyrrole despite the existing differences in oxidation potentials and other chemical properties which suggests the potentially extensive applicability of these electrochemical processes. The in situ reflection spectra at the Pt/poly-1/PMeT electrodes were measured with a normally incident light beam led by fiber optics in TBAP/acetonitrile solutions during the CV sweeps at 50 mV s^{-1} using a MCPD-100 Multi-Channel Photo Detector (Ohtsuka Denshi Co.). The results are shown in Fig. 2. Each spectrum is based on the accumulated signal obtained by 8 repeated wavelength sweeps with a gate time of 12 ms each. This means that each spectrum is obtained over ca. 5 mV. From Fig. 2, it is evident that by a potential sweep, $1 \longrightarrow 2 \longrightarrow 3 \longrightarrow 4 \longrightarrow 5 \longrightarrow 6 \longrightarrow 7$, reversible optical switchings occur when the potential is swept across the sharp CV waves. Hence, Fig. 2 should be another evidence for the mediated electrochemical doping and undoping reactions of PMeT. The forward (doping) optical switching ($1 \longrightarrow 2$) is observed as the disappearance of the absorption band at ca. 480 nm, and the evolution of the absorption band for $\lambda > 560$ nm. The former absorption band has been ascribed to the interband transition.1a,3) A small backward increase in absorption below 560 nm is observed for $2 \longrightarrow 3$, while for 560 nm $< \lambda <$ 870 nm the absorption also

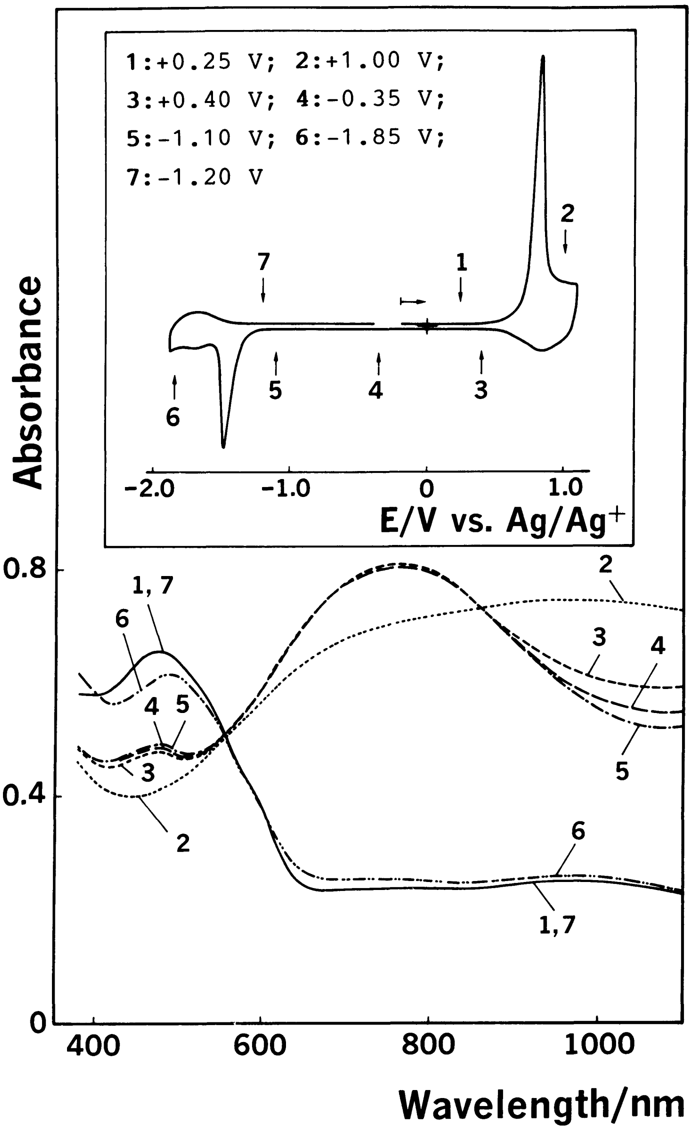

Fig. 2. In situ reflection spectra of Pt/poly-1/poly-3-methylthiophene bilayer electrode immersed in 0.1 M TBAP/acetonitrile during potential sweeps (inset). Each spectrum is based on the accumulated signal (8 samples) gated at 12 ms each. Scan rate: 50 mV s^{-1}.

increased. Throughout these changes, the isosbestic point is maintained. The absorption change by the inner layer upon the doping sweep for λ>560 nm is negligible, confirmed by testing the electrodes with various coverages of the inner layer. This 'unparalleled' behavior is anomalous and cannot be explained by the charge leakage between the outer layer and platinum substrate. During the sweep **3** ⟶ **5**, absorption below 560 nm is only slightly changed, while for 870 nm< λ the absorption decreased. Well-defined band maxima centered at 680 nm and at 1000 nm are often observed in spectrum **2** among a number of tested electrodes. It has been reported on polythiophene[1c)] and PMeT[2)] that absorption bands are evolved in the same regions at low doping levels (<1%) and are assigned to polaronic transitions. They also assigned the absorption bands at 760 nm, which appear at the higher doping levels, to be due to bipolarons. Interestingly, the spectra **3**, **4**, and **5** in Fig. 2 also have band maxima at the same wavelength. Hence the spectral changes in Fig. 2 are understood as follows; the polaronic states are predominant in **2**, but are transformed to bipolarons during the sweep of **2** ⟶ **3**. Most of the optical studies so far reported on the electrochemically generated mid-gap states of polythiophenes have been performed under static conditions based on relatively thicker films (~μm). In contrast, the spectra of Fig. 2 represent dynamic processes in the course of achieving equilibrium within the PMeT layer. This scheme is enabled by the configuration in which the relatively thinner PMeT layer (<100 nm) is isolated from the substrate by the intervention of an electrically insulating, but electrochemically active inner layer. The detailed results will be published in full form.

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