Control of the Redox Behavior of Polypyrrole by Magneto-Electropolymerization

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The redox behavior was investigated of a p-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) film electrochemically polymerized in magnetic fields. It was found that the magnetic fields higher than 1 T drastically changes the redox potential into the more negative side. The redox behavior was also controlled by the hybridization of the PPy/TsO$^-$ films polymerized with and without magnetic field.

Polypyrrole (PPy) is of great potential interest in connection with a functional molecular device, and its functionality depends on the morphology including a dopant anion.[1-4] While a PPy film containing a spherical anion (*e.g.* NO_3^-, ClO_4^- and BF_4^-) as the dopant has an isotropic molecular organization and a redox potential of 0 ~ 0.1 V (vs Ag/ AgCl), a p-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) film has an anisotropic organization, where the planes of aromatic rings lie preferentially parallel to the electrode surface.[5,6] The PPy/TsO$^-$ film has the redox potential of -0.4 ~ -0.5 V and exhibits a characteristic reduction (undoping) peak at -0.5 ~ -0.6 V in a cyclic voltammogram (CV) in a TsONa aqueous solution.[1,3]

It is well known that most organic polymers have so large anisotropy in a diamagnetic susceptibility that they are subject to the diamagnetic orientation, resulting in the morphological changes, in magnetic fields.[7,8] In previous papers[9,10] we reported that the magnetic field causes the oriented polymerization of PPy/TsO$^-$, resulting in the drastic morphological change, and that the PPy/TsO$^-$ film polymerized in the magnetic field of 12 T loses the electrical plastic behavior in the dopant-exchange process during the redox cycle of -0.5 ~ 0.5 V in a $LiClO_4$ aqueous solution. In this paper we examine that the magneto-electropolymerization (electrochemical polymerization in magnetic fields) is able to control the redox potential or other redox behavior of the PPy/TsO$^-$ film.

The magneto-electropolymerization of pyrrole was carried out at 20 °C using an electrochemical analyzer BAS-100B/W and the Bitter-magnet in the High Field Laboratory of Tohoku University. The electrode system consisted of a platinum disk (ϕ1.6 mm) as a working electrode, a Ag/AgCl electrode as a reference one and a platinum plate as a counter electrode. The PPy/TsO$^-$ film was polymerized at a constant potential of 1.0 V by 1.0 C cm^{-2} on the platinum-disk electrode in a 0.1 M (M = mol dm^{-3}) pyrrole aqueous solution containing 0.1 M TsONa. The magnetic field was applied up to 12 T perpendicularly to the surface of the working electrode and parallel to the faradaic current to eliminate the magnetohydrodynamic effect as described.[11] The CV's of the films were measured with a sweep rate of 50 mV s^{-1} in a 0.1 M TsONa aqueous solution in the absence of magnetic field.

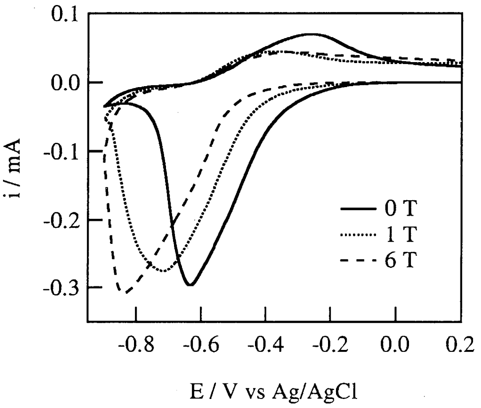

Figure 1. Cyclic voltammograms of the PPy/ TsO$^-$ films polymerized in 0 T, 1 T and 6 T. The CV's were measured with a potential sweep rate of 50 mV s^{-1} in a 0.1 M TsONa aqueous solution in the absence of magnetic field.

Figure 1 shows the CV's of the PPy/TsO$^-$ films polymerized in 0 T, 1 T and 6 T. A characteristic reduction peak at -0.63 V of the 0T-film, corresponding to the undoping process of TsO$^-$, shifts to the more negative potentials in the 1T- and 6T-films. An oxidation peak also shifts to the negative potentials and gets smaller in the magneto-electropolymerized films, implying that the doping reaction becomes slower. The undoping peak potential E_{pc} of the films were plotted as a function of the magnetic field B in Figure 2. The peak potential drastically changes around 1 T and it is surprising that the potential shift goes up to -200 mV for the 6T- and 12 T-films. We have made similar experiments in a PPy/ClO_4^- system, and but such prominent effects were unobservable in the magneto-electropolymerized PPy/ClO_4^- films.

Our previous paper[9] showed that PPy/TsO$^-$ grows into an open-ramified fractal pattern in 0 T and a closed pattern in 0.5 T. The micrograph of the latter showed that the organization of the polymer is dense aggregates of needle-like branches, resulting from the diamagnetic orientation of the aromatic planes. The magneto-electropolymerized PPy/TsO$^-$ film is thus considered to be so rigid that the higher energy is necessary for the migration of the dopant anions within the film, resulting in the negative shift of the undoping peak potential. The PPy/TsO$^-$ film has the anisotropic organization, in which both the PPy layers and the

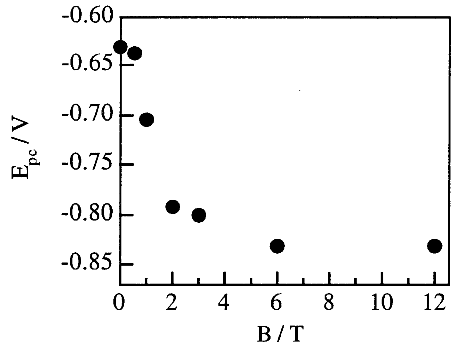

Figure 2. Cathodic peak potential E_{pc} in the CV of the PPy/TsO$^-$ films versus the magnetic field B in which the films were polymerized.

Table 1. The redox behavior of the hybrid PPy/TsO$^-$ films prepared with and without magnetic field

Film	Q^a / C cm^{-2} inner	Q^a / C cm^{-2} outer	$E_{1/2}{}^b$ / V	ΔE^c / V
1	0.50 (6T)	0.50 (0T)	-0.54	0.43
2	0.50 (0T)	0.50 (6T)	-0.54	0.57
3	0.25 (6T)	0.75 (0T)	-0.46	0.48
4	0.75 (0T)	0.25 (6T)	-0.48	0.58

^{a}Deposition charge. ^{b}Redox potential. ^{c}Potential difference between the cathodic and anodic peaks.

aromatic plane of the dopant TsO$^-$ lie nearly parallel to the electrode surface.[5] The influence of the diamagnetic orientation is most effective on such a structure, because the magnetic field is applied perpendicularly to the electrode surface in the present experiment and the aromatic plane is liable to orient parallel to the magnetic field.

We have tried to control the redox behavior of the PPy/TsO$^-$ film by hybridization of the films polymerized with and without magnetic field. We prepared four hybrid films as given in Table 1, where the films **1** and **3** consist of the inner layer polymerized in 6 T and the outer layer polymerized in 0 T, the films **2** and **4** are hybridized reversely. The total deposition charge of all the films is 1.0 C cm^{-2}. The CV's of the films **1** and **2** are shown in Figure 3, and the redox potential $E_{1/2}$ and the potential difference between the cathodic and anodic peaks ΔE of all the films are summarized in Table 1. It is noted that the films **1** and **2** have the nearly same redox potential, and the CV of the film **2** however is more irreversible. A similar result is obtained in the films **3** and **4**. These results imply that the magneto-electropolymerized outer rigid layer reduces the flexibility for the undoping and doping processes, causing the large irreversibility in the films **2** and **4**.

In conclusion we have shown that the magneto-electropolymerization and the hybrid-polymerization with and without magnetic field are able to control the redox potential and irreversibility of the PPy/TsO$^-$ film.

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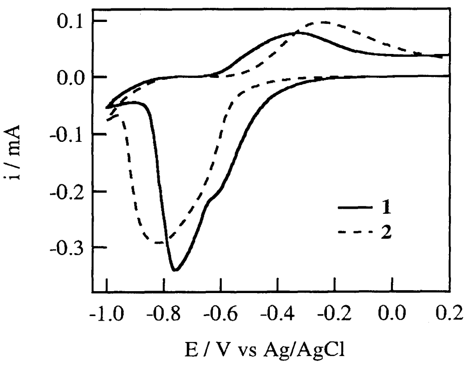

Figure 3. Cyclic voltammograms of the hybrid PPy/TsO$^-$ films **1** and **2** listed in Table 1. The CV's were measured with a potential sweep rate of 50 mV s^{-1} in a 0.1 M TsONa aqueous solution in the absence of magnetic field.

References and Notes

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