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Effects of Magnetic Field on Electropolymerization of Pyrrole

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Electropolymerization under a magnetic field (magneto-electropolymerization) is an interesting method to prepare conductive polymers. It is well known that a *p*-toluenesulfonate-doped polypyrrole (PPy/TsO$^-$) film has a large anisotropic organization with layered structures of the aromatic rings parallel to the electrode when prepared without magnetic field. This layered structure is reduced slightly if a magnetic field is applied during electropolymerization in the direction parallel to the electric filed. This is due to the diamagnetic anisotropy of the aromatic rings. In this paper the angle of the working electrode was chosen as 0° or 90° with respect to the direction of the magnetic field in order to study the effect of magnetic field on the film structure. A quasi-closed cell was used for the electrode system in order to eliminate the magnetohydrodynamic effect and to separate it from the effect of diamagnetism of aromatic rings. The analyses of the surface morphology and the bulk structure were carried out.

Key words: Magnetic Field, Pyrrole, Electropolymerization, Magnetic Orientation, Surface Structure

1. INTRODUCTION

Polypyrrole (PPy) film has drawn attention because of its good environmental stability and relatively high electrical conductivity. Magneto-electropolymerization is an interesting method to control the bulk structure, surface morphology, and redox behavior of PPy because the magnetic field affect on polymerization process through anisotropic diamagnetic susceptibility of PPy. Mogi *et al.* reported the magnetic field effects on the fractal growth morphology of electroless-deposited and electrodeposited metals [1, 2] and electropolymerized conductive polymers [3, 4]. It is well known that a PPy/TsO$^-$ film has a large anisotropic organization with a layered structure of the aromatic rings aligned parallel to the electrode when prepared in 0 T. Therefore, it is expected that the magnetic field is most effective to the orientation of polymer chains if it is applied parallel to the electrode surface. In this paper the angle of the working electrode surface was chosen as 0° (in this case magnetohydrodynamic (MHD) effect [5, 6]) or 90° (no MHD effect arise) in order to study in detail the effect of

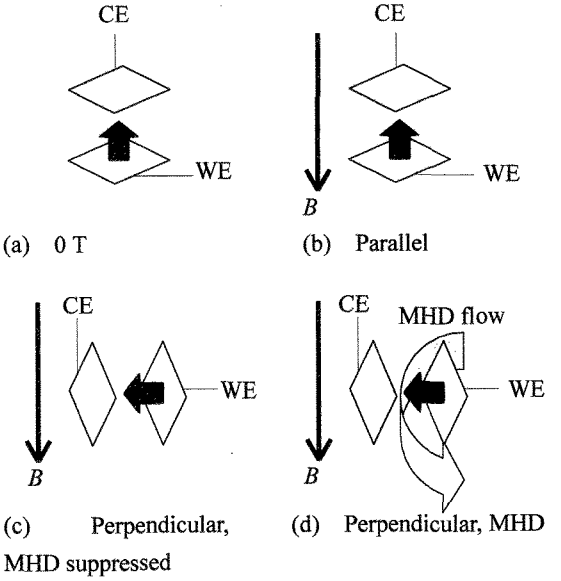

Fig. 1 Relationship between the directions of the electric current and the magnetic field.
WE: working electrode, CE: counter electrode

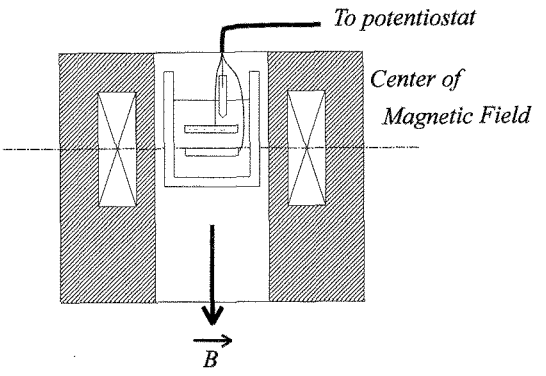

Fig. 2 Experimental setup of the electrochemical cell.

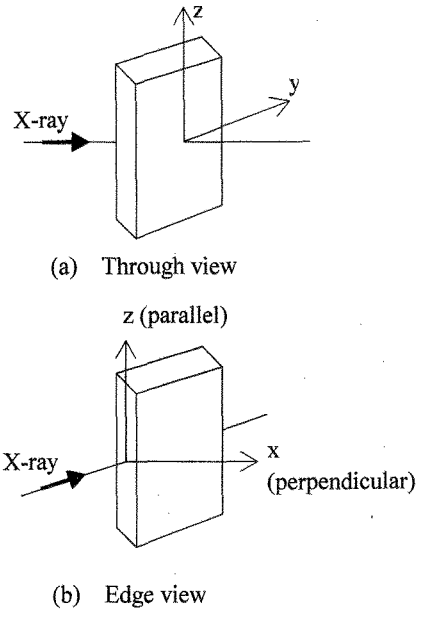

Fig. 3 The X-ray scattering geometry.

magnetic field on the film structure. To reduce the MHD effect and hence to separate the effect of magnetic field on alignment of the polymer chain, a step potential method with a quasi-closed cell was used. Surface morphology and bulk structure were analyzed.

2. EXPERIMENTAL

All chemicals were of guaranteed reagent grade. The PPy film was prepared by electrochemical oxidation of pyrrole monomer. This was carried out in a one-compartment cell using a Toho Technical Research (TTR) 2000 potetiostat/galvanostat equipped with a TTR FG-02E function generator and personal computer.

The electrode system consisted of an ITO glass (1 × 1 cm^2) as a working electrode, an Ag/AgCl electrode as a reference one, and platinum plate (1.2 × 1.2 cm^2) as a counter electrode, as shown in Fig. 1. The PPy/TsO^- film was prepared on the ITO glass electrode by electropolymerization at step potential (1.0 V, 3 sec.) in a 0.1 M (1 M=1 mol dm^{-3}) pyrrole aqueous solution containing 0.1 M TsONa as a supporting electrolyte. The numbers of step potential was 300 steps for the sample used for X-ray diffraction method. Sample under MHD condition was prepared by electropolymerization at a constant potential (1.0 V).

The electrochemical cell was placed in the center of the magnet, and temperature within the magnet was controlled to be at 20°C by using a water-circulating thermoregulator, as shown in Fig. 2.

The film surface of PPy/TsO^- was observed by

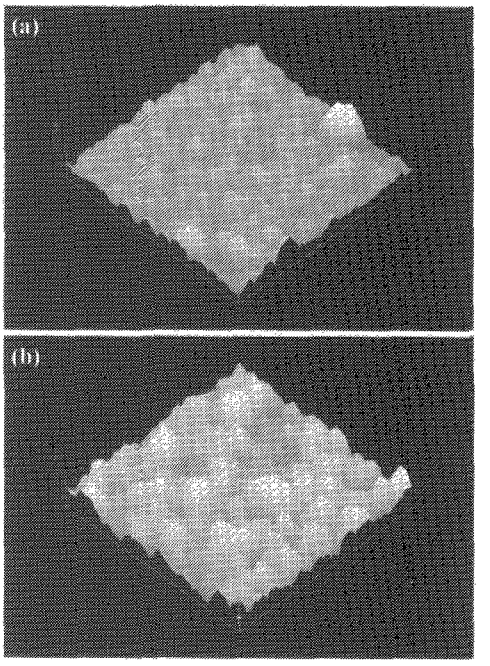

Fig. 4 AFM images of PPy/TsO^- film at ITO glass electrode. (a); 10 T (perpendicular, MHD suppressed), (b); 10 T (perpendicular, MHD).

Table I Average roughness (nm) of PPy/TsO^- films surface.

	0 T	10 T (MHD suppressed)	10 T (MHD)
0.17 C/cm^2	5.8	5.6	9.6

means of atomic force microscopy (AFM) to confirm the existence of a MHD flow. The roughness of PPy/TsO$^-$ film surface was numerically estimated on the basis of Japanese Industrial Standards (JIS) [7].

The wide angle X-ray diffraction patterns (using Cu Kα radiation) were measured with scattering geometry, as shown in Fig. 3.

3. RESULTS AND DISCUSSION

Fig. 4 shows AFM images (5 μm) of the electrode surfaces modified by the electropolymerization in 10 T under the experimental condition (a) perpendicular, MHD suppressed, "step potential" and (b) perpendicular, MHD; "constant potential".

The roughness of PPy film surface was numerically estimated and shown in Table I. In the case with a MHD flow, the morphology of the modified electrode surface differs from that of the surface modified by the electropolymerization in 0 T. The roughness of the sample electropolymerized in 10 T (perpendicular, MHD suppressed) is similar to that for the sample prepared in 0 T, indicating that the suppression of the MHD effect is attained by the use of quasi-closed cell.

The wide angle X-ray diffraction pattern of PPy/TsO$^-$ film in 9 T (parallel) is shown in Fig. 5. Diffractograms of PPy/TsO$^-$ film usually show a maximum around 2θ=6~7° region, which is attributed to diffraction due to counter-anions [8, 9], whilst the maximum at 2θ=25~26° originates from the spacing between pyrrole rings [8, 10]. Although the magnetic field was applied perpendicularly to the surface of the working electrode, the layered structure of PPy lies parallel to the electrode surface.

Fig. 6 shows the X-ray azimuthal scans carried out in the edge view at 2θ=26° for PPy/TsO$^-$ films to estimate the degree of orientation. The degree of orientation of the sample electropolymerized in 9 T (parallel to the electric field) is lower than that prepared in 0 T. This suggests that the magnetic field reduces layered organization of the aromatic rings aligned parallel to the electrode.

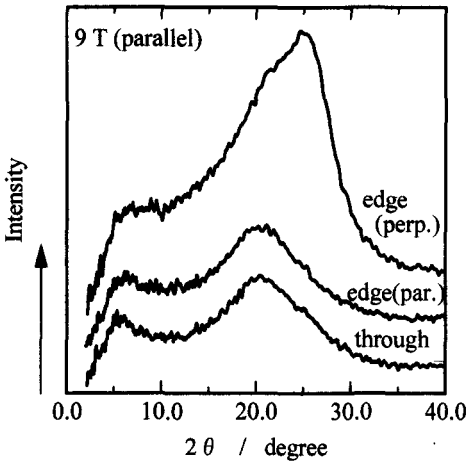

Fig. 5 The wide angle X-ray diffraction pattern of PPy/TsO$^-$ film prepared in 9 T (parallel).

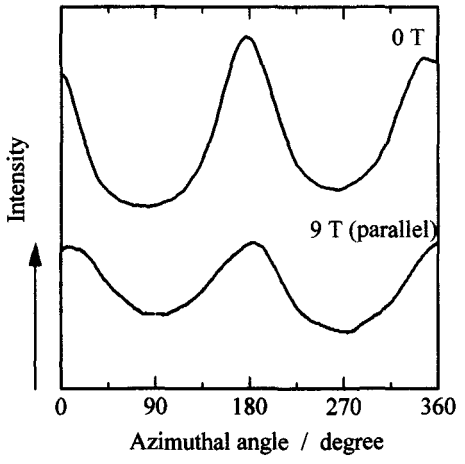

Fig. 6 The X-ray azimuthal scans at 2θ=26° of edge view for PPy/TsO$^-$ films.

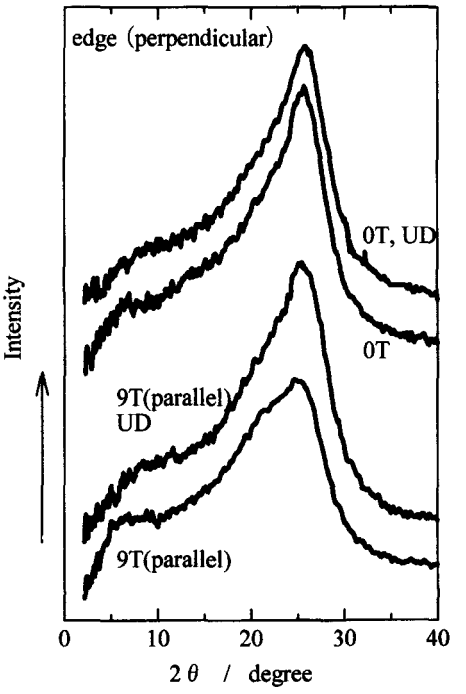

Fig. 7 The wide angle X-ray diffraction pattern of PPy/TsO$^-$ film. UD; undoping.

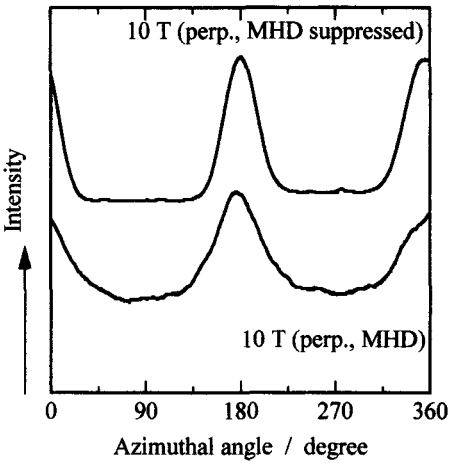

Fig. 8 The X-ray azimuthal scans at 2θ=26° of edge view for PPy/TsO$^-$ films.

The decrease of anisotropic organization parallel to the electrode is recovered upon undoping in the absence of the magnetic field, as shown in Fig. 7. Here, the undoping process of PPy/TsO$^-$ films was carried out in a 0.1 M TsONa aqueous solution at 1.0 V (vs. Ag/AgCl).

The wide angle X-ray diffraction pattern of PPy/TsO$^-$ film prepared in 9 T (parallel) followed by undoping exhibits the same shape as PPy/TsO$^-$ film electropolymerized in 0 T. This suggested that the anisotropic organization parallel to the electrode is recovered upon undoping.

Fig. 8 shows the edge view azimuthal scans at 2θ=26° for PPy/TsO$^-$ films. The degree of orientation of the sample electropolymerized at 10 T in the condition "perpendicular, MHD suppressed" is higher than the condition "perpendicular, MHD". This suggests that the MHD effect is not favorable to the magnetic orientation.

4. CONCLUSIONS

The direction of the magnetic field has an effect on the structure morphology of the PPy films electropolymerized in the magnetic fields. The degree of orientation of the sample electropolymerized in the condition "parallel to the electric field" is higher than the condition "perpendicular to the electric field, MHD suppressed". The MHD effect is not favorable to the magnetic orientation.

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