

## Magnetic Alignment of Polypyrrole Layered Structures by Repeated Redox Cycles

Hiroyuki Morioka, Tsunehisa Kimura,\* and Ryoichi Aogaki<sup>†</sup>

*Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University,  
1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397*

*<sup>†</sup>Department of Product Design, Polytechnic University, 4-1-1 Hashimoto-dai, Sagami-hara, Kanagawa 229-1196*

(Received June 21, 2002; CL-020523)

A perchlorate-doped polypyrrole was processed by repeated redox cycles in a 0.1 M NaClO<sub>4</sub> aqueous solution under a magnetic field applied parallel to the faradic current. The film that was initially isotropic underwent magnetic alignment. X-ray measurement revealed that the polypyrrole layered structures were aligned perpendicular to the electrode surface.

Polypyrrole (PPy) film has drawn attention because of its good environmental stability and relatively high electrical conductivity.

A *p*-toluenesulfonate-doped polypyrrole (PPy/TsO) film exhibits an anisotropic structure in which the aromatic rings are aligned parallel to the electrode surface. This anisotropy is larger if the film is prepared using pulsed electrochemical potential than it is prepared under constant potential conditions.<sup>1-4</sup> Application of a magnetic field during the electropolymerization can align the polypyrrole layered structure and a resultant redox behavior of PPy/TsO films.<sup>5-11</sup> The magnetic field is assumed to act on aromatic rings, which have the anisotropic diamagnetic susceptibility, contained in the pyrrole/TsO system.

On the other hand, a perchlorate-doped polypyrrole (PPy/ClO<sub>4</sub>) film does not exhibit an isotropic structure irrespective of the electropolymerization conditions. The electropolymerization of PPy with 'spherical' anions such as BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> does not lead to anisotropic structures even if the pulse mode of electrochemical synthesis is used<sup>1-4</sup> or the magnetic field is applied during the electropolymerization.<sup>11</sup>

However, Mogi et al. reported that the degradation occurs if the polymerized PPy/ClO<sub>4</sub> film, prepared without magnetic field, is subjected to repeated redox cycles under a magnetic field in a potential range from 0.5 to -0.5 V with platinum electrode.<sup>6</sup> This degradation is probably due to the rearrangement of the polypyrrole chains occurring during the redox process. This rearrangement could suggest a possibility of alignment by means of post-processing of PPy/ClO<sub>4</sub> films.

In this paper, we show that the magnetoelectropolymerized PPy/ClO<sub>4</sub> film undergoes magnetic alignment if the film is subsequently subjected to the repeated redox cycles under a magnetic field. Unlike the work by Mogi et al., the cyclic voltammetry was carried out in this study in a wider potential range using an indium-tin oxide (ITO) glass electrode.

All chemicals were of guaranteed reagent grade. The PPy films were prepared by electrochemical oxidation of pyrrole monomer. The electrochemical polymerization reactions were carried out using a three-compartment cell connected to a Toho Technical Research (TTR) 2000 potentiostat/galvanostat equipped with a TTR FG-02E function generator and personal computer. An ITO (area 1 × 1 cm<sup>2</sup>) was used as the working electrode and a platinum plate as the counter electrode. All potentials were

measured with respect to the Ag/AgCl electrode.

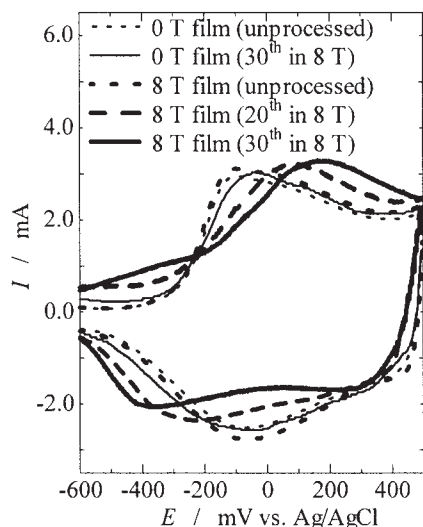
The PPy/ClO<sub>4</sub> films were polymerized onto the ITO glass electrode in a 0.1 M pyrrole aqueous solution containing 0.1 M NaClO<sub>4</sub> under a constant potential of 1.0 V. The polymerization was continued until the supplied charge reached 3.0 C·cm<sup>-2</sup>. The magnetic field was applied parallel to the faradic current to separate magnetohydrodynamic (MHD) effect<sup>12</sup> from the effect of magnetic field on alignment of the PPy layer. The MHD convection disturbs the film organization when the film is prepared at the MHD condition.<sup>10</sup> The electrochemical cell was placed in the magnetic field of 8 T generated by a cryocooler-cooled superconducting magnet (Sumitomo Heavy Industries Ltd., HF10-100VHT). The temperature within the magnet was controlled to be 20 °C by using a water-circulating thermostat. The PPy/ClO<sub>4</sub> film without application of magnetic field was also prepared.

Post-processing of the PPy/ClO<sub>4</sub> films by means of the repeated redox cycles under a magnetic field was carried out with a potential sweep rate of 50 mV·s<sup>-1</sup> in a 0.1 M aqueous solution of NaClO<sub>4</sub> in a potential range from 0.5 to -1.0 V. The magnetic condition was the same as aforementioned.

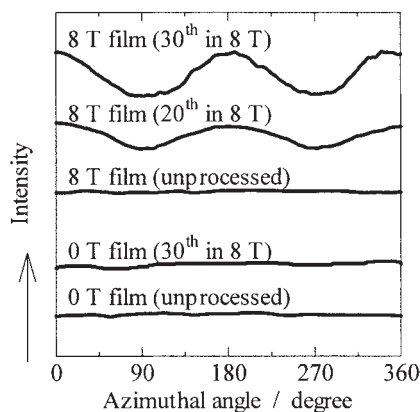
Wide-angle X-ray diffraction measurements were carried out with a MAC Science M18XHF-SRA equipped with an imaging plate. The schematic diagram of the experimental setup is described elsewhere.<sup>11</sup>

The voltammogram of the PPy/ClO<sub>4</sub> film polymerized under 0 T and post-processed in 8 T (0-T (30th in 8 T)) is almost identical with that of as-polymerized film (0-T (unprocessed)), as shown in Figure 1. Little effect of the post-processing is observed. Nor observed is the reported degradation<sup>6</sup> because the cycle number is small in the present study. On the other hand, a large effect of the post-processing is observed for the film polymerized under the magnetic field. The voltammogram of the film polymerized under 8 T (8-T (unprocessed)) shows a shift of peak position upon increase in cycles of the post-processing. This peak shift could be attributed to the accumulation of trapped cations within the films during the repeated redox cycles.<sup>6</sup>

Figure 2 shows the wide-angle X-ray azimuthal scans at 2θ = 26° of edge view for PPy/ClO<sub>4</sub> films to estimate the orientation. The diffraction at 2θ = 25° - 26° is attributed to the pyrrole layered structure, i.e., the spacing between pyrrole rings.<sup>13,14</sup> The field direction corresponds to the azimuthal angles 90° and 270°. The peaks at 0°, 180° and 360° indicate that PPy layered structure aligned perpendicular to the electrode surface. As-polymerized films, irrespective of the application of the magnetic field during polymerization, do not exhibit peculiar orientation of the pyrrole layered structure. Upon post-processing under magnetic field, the as-processed film prepared without magnetic field exhibits no increase in orientation, while that prepared under 8 T exhibits the increase in orientation. This



**Figure 1.** Cyclic voltammograms of the PPy/ClO<sub>4</sub> films which are prepared under 0 or 8 T and processed or unprocessed by repeated redox cycles in 0.1 M NaClO<sub>4</sub> aqueous solution in 8 T.

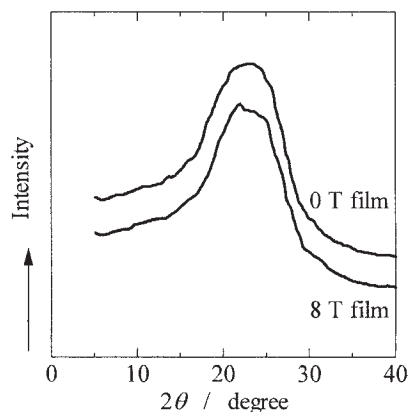


**Figure 2.** X-ray azimuthal scans of PPy/ClO<sub>4</sub> films at  $2\theta = 26^\circ$ . Sample names are the same as in Figure 1.

change in orientation is in accordance with the peak shift observed in the cyclic voltammograms shown in Figure 1. The change in molecular alignment could cause the change in dopant mobility, resulting in peak shift in the voltammograms.

Iseki et al. reported that an anisotropic molecular organization of PPy/TsO film changes to an isotropic one during redox cycles in a NaClO<sub>4</sub> aqueous solution.<sup>15</sup> They attributed this phenomenon to the molecular mobility enhanced by potential sweeping. Our observation of the increase in orientation by means of the post-processing might also be attributed to the enhanced mobility during redox cycle. However, the effect of the post-processing depends on how the as-polymerized films are prepared. This dependency could be attributed to the difference in the mobility of the pyrrole layered structures in as-polymerized films.

In Figure 3, the X-ray  $2\theta$  scans for the as-polymerized films (polymerized under 0 and 8 T) are shown. As mentioned before, the peak around  $2\theta = 25^\circ - 26^\circ$  is attributed to the pyrrole layered structure, while that around  $20^\circ$  is attributed to the



**Figure 3.** X-ray diffraction curves for the as-polymerized PPy/ClO<sub>4</sub> films prepared in 0 T and 8 T.

interdopant structure (pyrrole-dopant).<sup>16</sup> The as-polymerized film prepared under 8 T (8-T (unprocessed)) exhibits more contribution from interdopant structure than the film of the 0-T (unprocessed). Since the interdopant structure might be much mobile during the redox process, it would be expected that the mobility of the pyrrole layered structure is accordingly enhanced.

The perpendicular alignment of the pyrrole layered structure with respect to the electrode surface is attained by means of the post-processing of the magneto-electropolymerized PPy/ClO<sub>4</sub> film, resulting in the shift of the peak potential.

#### References

- 1 G. R. Mitchell, *Polym. Commun.*, **12**, 346 (1986).
- 2 G. R. Mitchell, F. J. Davis, and C. H. Legge, *Synth. Met.*, **26**, 247 (1988).
- 3 M. S. Kiani and G. R. Mitchell, *Synth. Met.*, **48**, 203 (1992).
- 4 M. S. Kiani, N. V. Bhat, F. J. Davis, and G. R. Mitchell, *Polymer*, **33**, 4113 (1992).
- 5 I. Mogi and M. Kamiko, *Denki Kagaku*, **64**, 842 (1996).
- 6 I. Mogi and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **70**, 2337 (1997).
- 7 I. Mogi, K. Watanabe, and M. Motokawa, *Electrochemistry*, **67**, 1051 (1999).
- 8 I. Mogi, K. Watanabe, and M. Motokawa, *Mater. Trans., JIM*, **41**, 966 (2000).
- 9 I. Mogi, K. Watanabe, and M. Motokawa, *J. Electroanal. Chem.*, **507**, 198 (2001).
- 10 H. Morioka, T. Kimura, and R. Aogaki, *Trans. Mater. Res. Soc. Jpn.*, **25**, 65 (2000).
- 11 H. Morioka, T. Kimura, and R. Aogaki, *Trans. Mater. Res. Soc. Jpn.*, **27**, 129 (2002).
- 12 R. Aogaki, K. Fueki, and T. Mukaibo, *Denki Kagaku*, **43**, 504 (1975).
- 13 K. J. Wynne and G. B. Street, *Macromolecules*, **18**, 2361 (1985).
- 14 L. J. Buckley, D. K. Royle, and G. E. Wnek, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 2179 (1987).
- 15 M. Iseki, K. Saito, K. Kuhara, and A. Mizukami, *Synth. Met.*, **40**, 117 (1991).
- 16 L. F. Warren, J. A. Walker, D. P. Anderson, C. G. Rhodes, and L. J. Buckley, *J. Electrochem. Soc.*, **136**, 2286 (1989).