

## Magneto-electropolymerized Polypyrrole Film Electrodes

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Control of chemical reactions by magnetic fields is one of current topics in high magnetic field science, which stemmed from the development and wide use of a cryocooled superconducting magnet. We have applied magnetic fields to the electropolymerization process (magneto-electropolymerization) of pyrrole in order to develop a novel technique for conducting polymer synthesis and electrode modification. Macromolecules with anisotropic magnetic susceptibility are subject to orientation in magnetic fields. Magneto-electropolymerization is expected to induce oriented polymerization, allowing control of their electrochemical properties. Here we report the redox behavior of magneto-electropolymerized polypyrrole (PPy) and some electrode reactions on such a PPy modified electrode.

The PPy films were electropolymerized on a Pt disk electrode at a constant potential 1.0 V (vs Ag/AgCl) in a 0.1 M pyrrole aqueous solution containing 0.1 M sodium p-toluenesulfonate (TsONa). Magnetic fields were generated up to 5 T by a liquid-He-free superconducting magnet with a large bore of 220 mm, the fields were applied parallel to the faradaic current to eliminate the magnetohydrodynamic convection. Electrochemical measurements with the PPy-TsO electrodes were done in the absence of a magnetic field.

The magneto-electropolymerization affects the morphology and the doping-undoping behavior of the PPy films [1]. The AFM images of the film surfaces demonstrate that small clusters of PPy as large as ~50 nm aggregate to form the 0T-film. On the other hand, the 5T-film is composed of large clusters as large as ~500 nm, each of which is a dense aggregate of small clusters. Such a dense structure and ac impedance measurements imply that the dopant mobility within the 5T-film is smaller than that in the 0T-film.

Cyclic voltammograms of both PPy-TsO films were measured in a TsONa solution (Fig. 1). The 0T-film exhibited two cathodic peaks at -0.47 and -0.6 V. From the electrochemical QCM measurements the former was assigned to the PPy reduction with anion undoping and the latter to the reduction with cation doping. On the other hand, the 5T-film exhibits only the latter peak. These results mean that at the PPy reduction process both anion undoping and cation doping occur in the 0T-film, while only cation doping occurs in the 5T-film.

Some electrochemical reactions were examined on modified electrodes with PPy-TsO in TsOH aqueous solutions. For example, both 0T- and 5T- films show good response for the redox reaction of anthraquinone-2-sulfonate around -0.1 V. It should be noted that the considerable difference was found for the proton reduction. Figure 2 shows the voltammograms of the proton reduction on the 0T-film and the magneto-electropolymerized films in a TsOH aqueous solution [2]. It is clearly seen that the electrode activity

for the proton reduction is decreased with increasing magnetic field during the polymerization. The result means that the proton reduction proceeds easily on the 0T-film and it hardly proceeds on the magneto-electropolymerized films. This effect is considered to arise from the diamagnetic orientation of the pyrrole planes in the MEP films.

### References

- [1] I. Mogi, K. Watanabe and M. Motokawa, *Electrochemistry*, **67**, 1051 (1999).
- [2] I. Mogi, K. Watanabe, and M. Motokawa, *Mat. Trans. JIM* **41** (2000) 966.

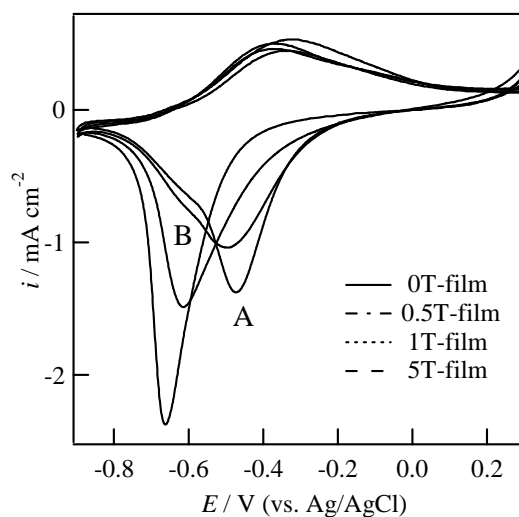


Fig. 1 CVs of the 0T-film and the magneto-electropolymerized films of PPy/TsO in a 0.1 M TsONa aqueous solution.

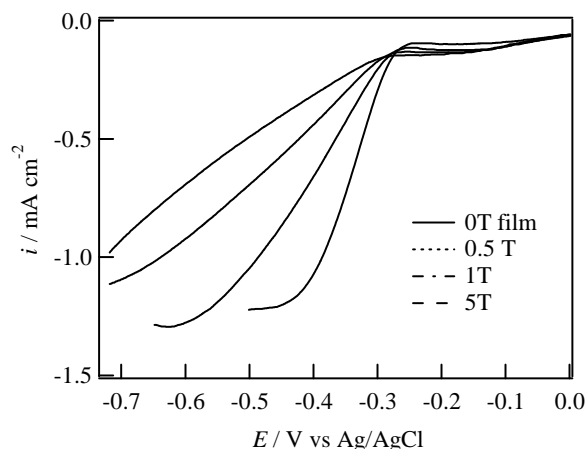


Fig. 2 Voltammograms of the proton reduction on the 0T-film and the MEP films of polypyrrole in a 0.1 M TsOH aqueous solution in the absence of a magnetic field.