Electrooxdative Copolymerization of Pyrrole with Bithiophene in Centrifugal Fields

Atsushi Murotani, Mahito Atobe and Toshio Fuchigami

Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

INTRODUCTION

In recent years, a variety of material processing has been carried out using high gravity centrifuge facilities.[1] On the other hand, electrochemical polymerization is also one of useful material processing and should be affected by the centrifugal acceleration force, and therefore the application of the force to the electrochemical polymerization is expected to be interesting investigation. In our previous work, centrifugal effects on the electrooxidative polymerization of aniline to lead formation of the corresponding electroconductive polyaniline film were examined in a range of 1 - 300 g of centrifugal acceleration force; the polymerization rate, chemical and physical properties and morphological structure of the film were greatly affected by the centrifugal field, and the effects occurred anisotropically with regard to direction of the force to a working electrode surface.[2] Subsequently, in this work, we demonstrated clear and significant centrifugal effects on the electrooxdative copolymerization of pyrrole with bithiophene leading to the formation of the corresponding copolymer film on the anode surface.

EXPERIMENTAL

Figure 1 shows centrifugal facilities equipped with a cylindrical electrolytic cell which is made with Teflon resin and has a 14 mm diameter and 7 mm length. Platinum discs (for working and counter electrodes) are electrically contacted with a galvanostat via silver rotating rings and carbon brushes. The entire cell assembly is suspended from the lid of a centrifuge tube with a polyethylene line. Surfaces of the platinum electrodes A and B faces inward and outward, respectively, to the centrifugal acceleration force, as shown in Figure 1. The forces on electrodes A and B are calculated to be about 315 and 290 g, respectively, at 1500 rpm. Electrode C is actually the electrode A at 1 g of the Earth gravity.

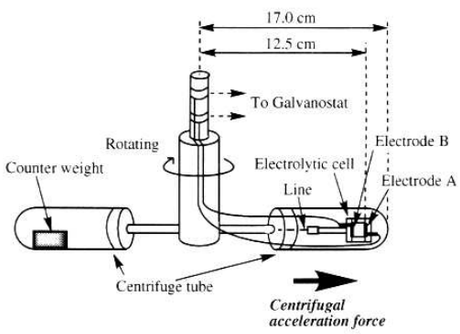

Fig.1. Centrifugal facilities equipped with an electrolytic cell.

Fig. 1. Centrifugal facilities equipped with an electrolytic cell.

After drying an electrolyte (0.1 M tetra-n-butylammonium perchlorate / CH_3CN) containing pyrrole (Py) / bithiophene (BT) comonomers with molecular sieve, it was injected into the cell. The concentration of each monomer was kept at 0.05 M. The electrooxdative copolymerization of Py with BT was carried out galvanostatically at 10 mA cm^{-2} by passing 11.34 C at room temperature. The proportion of Py units in the copolymer film deposited on the anode was determined using elemental analysis. The copolymer film was also subjected to scanning electron microscopy (SEM).

RESULT AND DISUCUSSION

Table 1 shows the proportion of Py units in the copolymer film prepared under Earth gravitational and centrifugal fields. The proportion of Py units was increased and decreased at centrifugal forces of 315 g and 290 g on electrodes A and B, respectively, compared with electrode C at 1 g. It should be noted again that the direction of the force to the surface of both electrodes is reversed. Therefore, it is suggested that the present anisotropical centrifugal effect was not caused by hydrostatic pressure approximately estimated to be about 1.2 and 1.0 atm on electrodes A and B, respectively, at 300 g. This interesting result can be explained in terms of the different specific densities of monomers (Py: 0.96 g cm^{-3} at 25 ^oC, BT: 1.05 g cm^{-3} at 25 ^oC) and their oligomers.

Table 1 Proportion of Py units in the copolymer film prepared under Earth gravitational and centrifugal fields

Gravity (g)	Proportion of pyrrole units in the copolymer film / mol %
1 g ; Electrode C	28.4
315 g ; Electrode A	23.2
290 g ; Electrode B	59.1

From SEM observation, it was also found that the surface morphology of the copolymer films is greatly affected by the centrifugal effect, i.e. the surface structure of films deposited on electrodes A and B is rough and smooth, respectively, compared with that on electrode C.

Thus, the centrifugal effect can be usefully applied to control the proportion of each monomer unit in a copolymer film and the morphology of films.

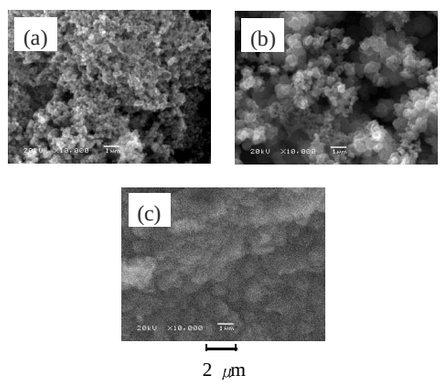

Fig. 2. SEM photographs of copolymer films of Py and BT polymerized at about (a) 1 g, (b) 315 g, (c) 290 g on electrode B.

References

1) L. L. Regel, W. R. Wilcox (Eds), *Materials Processing in High Gravity*, Plenum Press, New York, 1994.
2) M. Atobe, S. Hitose, T. Nonaka, *Electrochem. Commun.*, **1**, 278 (1999).