

Deposition of Polypyrrole on Microporous Filtration Membranes at Air/Water Interface

MYOUNGHO PYO, CHULAE CHO

Department of Chemistry, Sunchon National University, Suncheon, Chonnam 540-742, South Korea

Received 24 April 2001; accepted 30 August 2001

ABSTRACT: Microfiltration membranes were utilized as a template for the preparation of polypyrrole films at the air/water interface. Unlike the formation of polypyrrole tubules (or fibrils) when the membranes are soaked in polymerization media, chemical polymerization on the membrane at the interface resulted in the film formation on the membrane surface in contact with polymerization media, without remaining open micropores. Investigations of electrochemical responses with anthraquinone-2-sulfonate and $\text{Fe}(\text{CN})_6^{4-}$ on fully reduced or oxidized polypyrrole as well as studies of conductivity changes with polypyrrole deposition were carried out to confirm this behavior. Complete coverage of one side of a microfiltration membrane with a polypyrrole layer, remaining micropore walls, and the other side of a membrane intact, could be useful in various applications because it allows further electrochemical treatment/measurements utilizing these open micropores straightforward. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 514–518, 2002

Key words: electrochemistry; electron microscopy; membranes; polypyrroles

INTRODUCTION

Preparations of micro(nano)tubules and fibrils of various metals^{1–3} and conducting polymers^{4,5} has attracted considerable attention due to their potential applications in the area of physics, electronics, and materials science.⁶ A wide variety of approaches have been attempted using porous materials as a template such as filter paper,⁷ ion exchange membranes,⁸ nylon fabrics,⁹ zeolite,¹⁰ alumina,¹¹ and polycarbonate (PC) membranes.^{12–14} Utilizing PC membranes, Martin et al. have proposed a method to make the nanoelectrode ensembles by silanizing the pore wall and chemically depositing Au.¹³ They have also shown

that the tubules capped by polypyrrole can be used to load enzymes for the preparation of an enzymatic bioreactor.¹⁴

In addition to Au-coated PC membranes, conducting polymer films such as polypyrrole (PP), polythiophene, and polyaniline can also be used because they are directly synthesized on membranes. The reason for the nucleation and growth of the polymers is mainly due to solvophobic interaction of the polymer and the PC surface. It has been disclosed that the polymer preferentially deposits on the pore walls¹⁵ and the thickness depends on the polymerization time. These polypyrrole tubules can ultimately close up to form solid fibrils.¹⁶

In this article, we describe a new PP deposition method on PC membranes, in which the deposition is limited to one surface of a membrane and does not occur on the other surface or micropore walls. The conductivity and electrochemical studies as well as scanning electron microscopic

Correspondence to: M. Pyo (mho@sunchon.sunchon.ac.kr).
Contract grant sponsor: Korea Research Foundation.

Journal of Applied Polymer Science, Vol. 85, 514–518 (2002)
© 2002 Wiley Periodicals, Inc.

images clearly showed the formation of PP films that completely covered one side of a membrane. This method is distinct from PP-coated membranes made by immersion in the polymerization medium, which usually results in the formation of PP microtubules. The PP-coated membranes addressed here might be utilized for various applications such as the deposition of other conducting polymers in the open micropores by a second electrochemical deposition.

EXPERIMENTAL

Pyrrrole was passed over aluminum oxide until colorless before use. Sodium chloride, sodium anthraquinone-2-sulfonate, $K_4[Fe(CN)_6]$ (Aldrich), $FeCl_3$ (Oriental Chem. Ind., Korea), and HCl (Duksan, Korea) were used as received. Water was double distilled, having a resistance of 18 M Ω cm or higher. Polycarbonate (PC) membranes (Nuclepore) with a nominal pore diameter of 1 μ m and maximum pore density of $6 \times 10^8/cm^2$ were used as a template.

Oxidative chemical deposition of polypyrrole was carried out by placing PC membranes with a shiny face down on the surface of 1 mL aqueous solutions containing 0.15 M pyrrole and 1 M HCl, and subsequently flowing 1 mL solutions of 0.1 M $FeCl_3$ down along the wall. It should be mentioned that, although PP can be deposited either side, the film formed on the shiny side of a membrane is more homogeneous. In addition, because pyrrole dissolves the PC membrane, pyrrole concentrations should be maintained at lower than 0.15 M. For a comparative study, PP-coated membranes were also prepared by immersing membranes in pyrrole/HCl solutions and simply pouring $FeCl_3$ solutions to deposit PP on inner-pore walls as well as both sides of membranes, leading to the formation of PP microtubules.

After thorough washing and drying, the shiny face of a PP-coated membrane was affixed to and completely covered by adhesive Al foil tape (All-Foils Inc.). This was placed on a smooth Teflon plate, for the Al tape-treated face of a membrane to face on this plate. On top of it, the other Teflon plate with an opening of 0.71 cm², which allowed us to perform electrochemical measurements, was positioned and two Teflon plates were tightened up with screws. Therefore, the rough face of a membrane was always exposed to electrolyte solutions. The electrochemical experiments were performed using the BAS CV-50W with a conven-

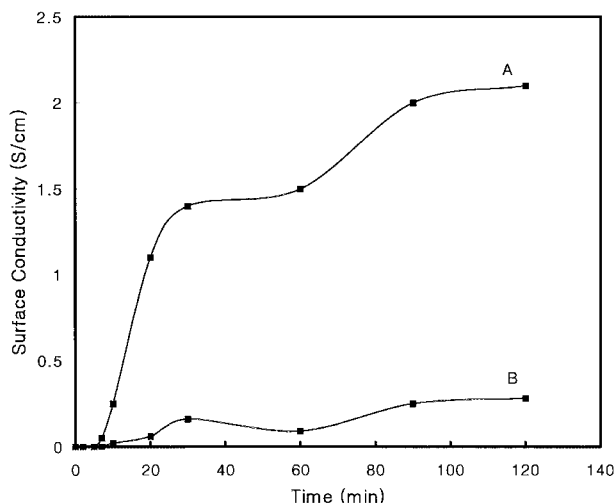


Figure 1 Conductivity changes of (A) shiny and (B) rough faces with polymerization times. The surface conductivity was measured by a conventional four-probe method.

tional three-electrode configuration. Ag/AgCl and Pt were utilized as reference and counter electrodes, respectively.

RESULTS AND DISCUSSION

During oxidative chemical polymerization of pyrrole, conductivity changes were examined for both faces of PC membranes by a conventional four-probe method. Figure 1 shows the changes of the surface conductivity with time when PP is synthesized on a membrane residing at the air/water interface. Although visual appearances of a membrane turn to gray within 5 min, no continuous PP phase is likely to be formed because the conductivity of either face is negligibly small. The conductivity of the shiny face, however, is abruptly increased to ca. 1.5 S/cm in between 5 and 30 min, and followed by a slight rise for a long period of time. On the other hand, the increase of the conductivity of the rough face that was exposed to air is relatively negligible, and remains at a much lower value than those of the shiny face. In case PP tubules are formed on microporous walls and reach the rough surface of a membrane, conductivity values are expected to be similar to those of the shiny face. Therefore, the conductivity differences shown in Figure 1 imply that PP deposition is restricted on a membrane face in contact with a polymerization medium and the formation of tubules is not likely to occur.

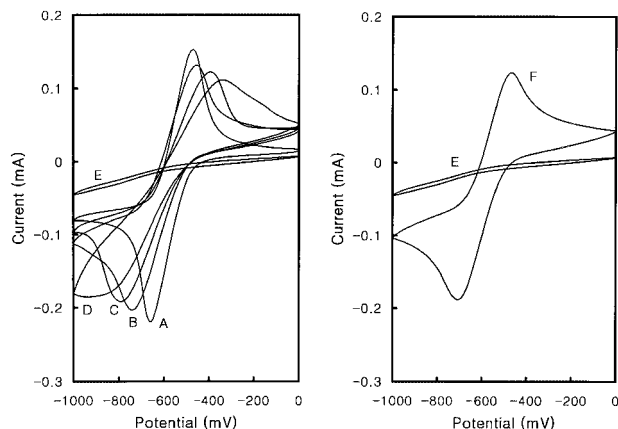


Figure 2 Cyclic voltammograms of PP-coated membranes in aqueous solutions containing 5 mM AQS and 0.1 M NaCl at 100 mV/s. The polymer was deposited on PC membranes at the air/water interface for (A) 0, (B) 20, (C) 30, (D) 60, and (E) 120 min, and (F) in a solution for 120 min.

To confirm the complete coverage of PP, the electrochemical responses of PP-coated membranes were investigated using anthraquinone-2-sulfonate (AQS) as a probe. Figure 2 shows cyclic voltammograms of PP-coated membranes prepared at various deposition times in an aqueous solution containing 5 mM AQS and 0.1 M NaCl. Because PP is in an insulating state at a potential window of AQS redox, it is believed that current responses result from the incomplete coverage of PP. As shown in Figure 2 (left), lengthening of the reaction time decreases peak currents and increases peak separations, indicating that electrochemically active area is becoming smaller with time. Electron transfer of AQS is completely blocked when PP is deposited for 2 h or longer. On the other hand, PP-coated membranes prepared by immersing PC membranes in the same polymerization media, are not likely to produce PP films, completely covering the one side of a membrane. Cyclic voltammograms of AQS on PP-coated membranes prepared at the interface and in a solution for 2 h were compared in Figure 2 (right). Although Figure 2E shows no current response of AQS redox, peak currents of Figure 2F is quite similar to those on a PP-free membrane shown in Figure 2A. Lengthening the PP deposition time does not change this behavior, demonstrating that the direct PP deposition on PC membranes at the air/water interface can be distinguished from other PP deposition methods known up to date.

To elucidate the absence of PP microtubules within micropores, electrochemical behaviors on PP-coated membranes were further examined by maintaining PP in an oxidized state. $\text{Fe}(\text{CN})_6^{4-}$ was utilized as an electrochemical probe. Figure 3 shows cyclic voltammograms performed on (A) a PP-free membrane and PP-coated membranes prepared (B) in a solution and (C) at the interface for 2 h. Peak currents on PP-coated membranes made in a solution [Fig. 3(B)] are ca. twice higher than those in Figure 3(A). This is not surprising, because PP coated on the rough face and pore walls exists in a conducting state during $\text{Fe}(\text{CN})_6^{4-}$ redox, and can function as a substrate for electron transfer. On the contrary, similar voltammetric responses were revealed between PP-free membranes [Fig. 3(A)] and PP-coated membranes prepared at the interface [Fig. 3(C)]. This result indicates that the formation of tubules, which should increase electrochemically active areas, did not occur. Furthermore, because the comparison of cyclic voltammograms before complete coverage of PP with Figure 3(A) showed no significant increase of $\text{Fe}(\text{CN})_6^{4-}$ redox, the possibility of the fibril formation of appreciable lengths was excluded.

Chronoamperometric measurements were carried out to compare the electrochemically active areas that can be related to PP surface areas

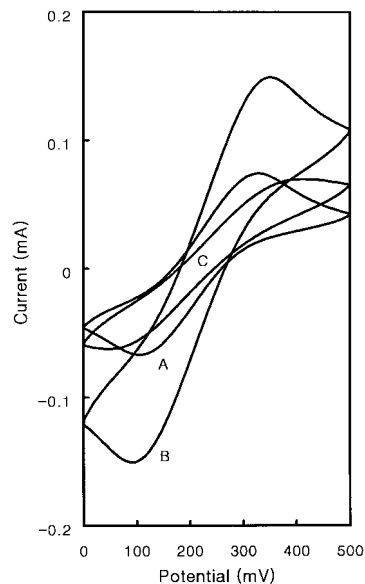


Figure 3 Cyclic voltammograms in aqueous solutions containing 5 mM $\text{Fe}(\text{CN})_6^{4-}$ and 0.1 M NaCl at 100 mV/s for (A) a PP-free membrane and PP-coated membranes prepared (B) in a solution and (C) at the interface.

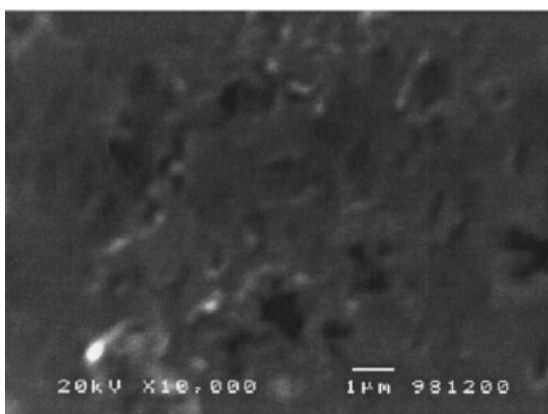
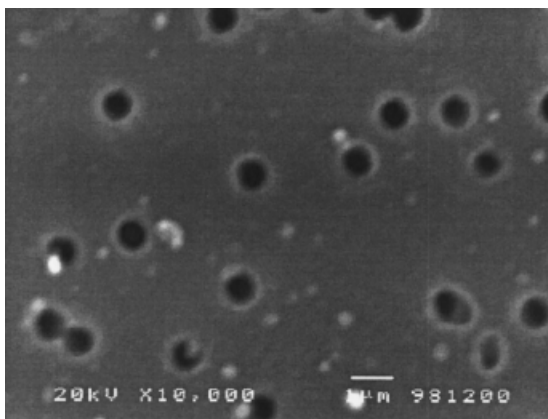


Figure 4 Scanning electron microscopic images of PC membrane faces (top) exposed to air and (bottom) contacted to polymerization media during chemical deposition of PP for 120 min.

exposed to the solution containing electroactive species. Current changes were monitored after applying a step potential from +500 to 0 mV in a solution of 5 mM $\text{Fe}(\text{CN})_6^{4-}$ and 0.1 M NaCl. Assuming semi-infinite linear diffusion, the active areas were figured out to be 0.061, 0.125, and 0.054 cm^2 for a PP-free membrane and PP-coated membranes, in which PP coated in a solution (2-h deposition) and PP coated at the interface (2 h deposition), respectively. Again, these values correspond to the cyclic voltammetric result shown in Figure 3.

Scanning electron microscopic images were obtained for either side of PP-coated membranes (Fig. 4). The pictures show that, while one side remains intact, the other is covered by PP completely.

CONCLUSIONS

PP-coated microporous membranes, in which the PP deposition is restricted to one face of a membrane, were readily prepared by placing PC membranes at the surface of polymerization media. PP-coated membranes, prepared at the interface, were examined by electrochemical and microscopic methods. The fact that such a PP deposition results in the complete coverage of one face of membranes without forming microtubules on the pore walls, makes this approach distinctively differ from ones made by immersing membranes in

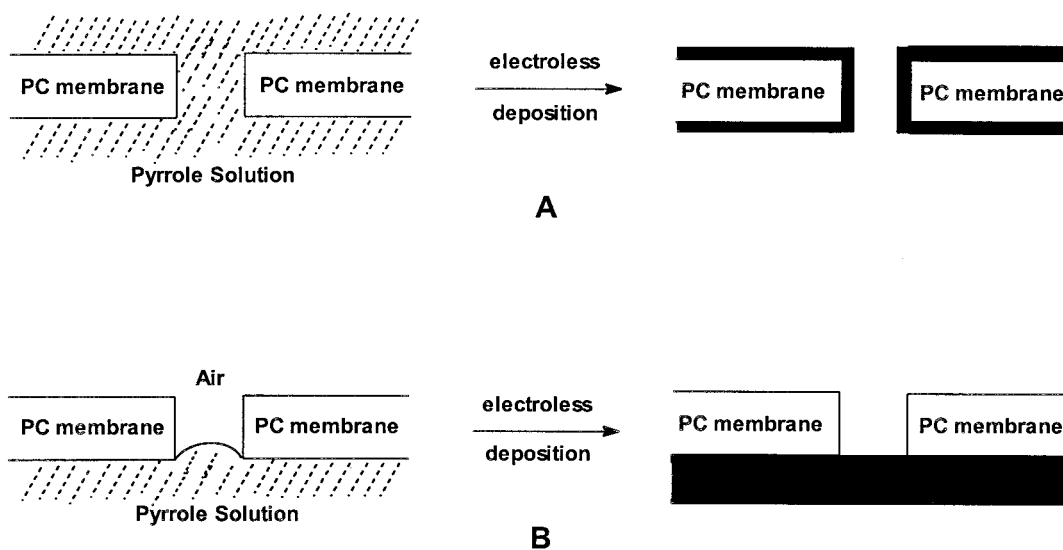


Figure 5 Schematic representation comparing the concept of PP deposition (A) in a solution and (B) at the interface.

solutions. A schematic illustration of PP film formation is shown in Figure 5.

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998.

REFERENCES

1. Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Science* 1997, 278, 655.
2. Brumlik, C. J.; Martin, C. R. *Anal Chem* 1992, 64, 1201.
3. Brumlik, C. J.; Menon, V. P.; Martin, C. R. *J Mater Res* 1994, 9, 1174.
4. Lee, H. S.; Hong, J. *Synth Met* 2000, 113, 115.
5. Vito, S. D.; Martin, C. R. *Chem Mater* 1998, 10, 1788.
6. Martin, C. R.; Mitchell, D. T. *Anal Chem (News Features)* 1998, 323A.
7. Bjorklund, R. B.; Lundstrom, I. *J Electron Mater* 1984, 13, 211.
8. Sata, T. *J Membr Sci* 1992, 66, 289.
9. Martin, C. R. *Science* 1994, 266, 1961.
10. Wu, C.-G.; Bein, T. *Science* 1994, 264, 1757.
11. Foss, C. A., Jr.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *J Phys Chem* 1992, 96, 7497.
12. Nishizawa, M.; Menon, V. P.; Martin, C. R. *Science* 1995, 268, 700.
13. Menon, V. P.; Martin, C. R. *Anal Chem* 1995, 67, 1920.
14. Parthasarathy, R.; Martin, C. R. *Nature* 1994, 369, 298.
15. Martin, C. R. *Adv Mater* 1991, 3, 457.
16. Parthasarathy, R.; Martin, C. R. *Chem Mater* 1994, 6, 1627.