

POLYMERIZATION KINETICS AND CHARACTERIZATION OF POLYPYRROLE MICROTUBULES FORMED INSIDE THE PORES OF POROUS MEMBRANES

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In the present article, synthesis and characterization of polypyrrole (PPy) microtubules formed in the pores of polycarbonate (PC) membranes are discussed. Electropolymerization and polymerization kinetics of pyrrole in the pores of PC membranes and tubule formation have been elucidated with the help of scanning electron microscopy (SEM). *In situ* conductance measurements at various polymerization time are discussed relating conductance between two side of the membrane with the growth of polymer tubules.

Key Words : Conducting Polymers; Electropolymerization; Interfacial; Electron Microscopy

Introduction

In the field of microelectronics, there is a great interest in the use of conducting polymers in nano or micrometer sized devices due to their interesting electronic, optical and mechanical properties. Recently synthetic capabilities as well as fabrication techniques have been developed to such an extent that molecular electronic devices based on conducting polymers can be designed and fabricated. An important area of application for these materials is the development of sensors for chemical and biochemical species¹⁻⁴. Polymer materials with low dimensionality can be prepared using various techniques. The use of track-etched membranes as templates seems to be a particularly interesting approach to synthesize polymer tubes with nanometric dimensions. We have adapted the idea of Martin *et al.*⁵ to use 'track-etched' isoporous polycarbonate membranes to fabricate PPy microtubules. Using this polymer microtubules sensor and sensor array have been designed and fabricated⁶. The sensitivity of these sensors depends on the morphology of the polymeric tubules inside the pores of the membrane. The morphology of the electropolymerized material strongly depends on the polymerization conditions. Therefore, it was an interesting area to study the polymerization kinetics inside the pores of the membrane.

The 'track-etched' pores are cylindrical and have a very narrow pore size distribution. The pores act as templates for the deposition of polymers on such

membranes. The properties of polymer tubules can be modulated by changing the properties of the pore walls⁷. Electrochemical template synthesis can be done by coating the surface of the membrane with a metallic film. This metal film will act as an anode for the electrochemical synthesis of the polymer. The polymer nucleates and grows on the pore walls giving polymeric tubules. By controlling the polymerization time we can obtain tubules with thin or thick walls.

In this report the kinetics of polymerization of PPy tubules growing from one side of the membrane is described as occurring in four stages. SEM images, recorded at various polymerization times, show the growth of polymer on the membrane surface and through the pores of the membrane. *In situ* conductance measurements at various polymerization times also describe the growth of polymer inside the pores of the membrane.

Experimental

Chemicals

Pyrrole was distilled under nitrogen atmosphere and only freshly distilled pyrrole was used to prepare monomer solutions. The aqueous monomer solution was stored at low temperature ($\sim 6^\circ\text{C}$) under N_2 atmosphere. The solution turns yellow if stored for a long time (more than a month). Colourless pyrrole solutions were used to obtain reproducible electroactive polymer films. Salts used for buffer solution were GR grade from Merck and used without further purification. All solutions were

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prepared using deionised water, which was further purified by a Milli Q microfiltration system.

Membrane Based Electrode

Polycarbonate (PC) membranes from Millipore Corporation were used to fabricate electrodes. Studies were carried out with membranes having pores of 1.2 μm diameter. Thickness of these membranes is 10 μm . Gold lines (thickness 800-1000 \AA and width about 1 mm) were deposited on the both sides of the membrane by using an aluminum mask during gold evaporation. The gold evaporation was done by a homemade vacuum evaporation system in Department of Physics, IIT Bombay. The mask was made by cutting equidistant lines of 1 mm width separated by 1 mm on an aluminum sheet with a circular cutting blade at the Machine Tools Workshop of Department of Mechanical Engineering, IIT Bombay. During gold evaporation, the mask was aligned in such a way that each gold line was exactly superimposed on the corresponding line on the other side of the membrane. Each gold line was used as an Electrode. Fig. 1 shows a gold coated and an as supplied membrane, and the inset shows a magnified picture of the membrane pores.

Electropolymerization

Electropolymerization was carried out under N_2 atmosphere in a three-electrode cell. The working electrode was a gold-coated PC membrane (Au-PC) held by a small clip holder having Pt strips on both sides for electrical contact. A Saturated Calomel Electrode (SCE) and a Pt foil were used as reference and counter electrodes respectively.

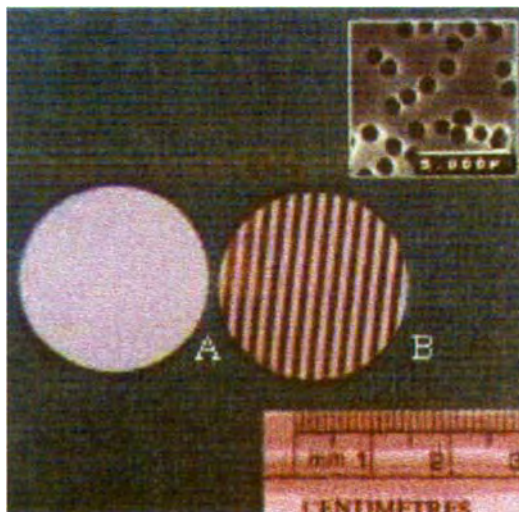


Fig. 1 Bare (A) and Gold coated (B) membrane with pores. Inset shows magnified membrane pores

The gold surface was cleaned by cycling the potential between -0.2 to +1.6 V vs. SCE in 0.5 M H_2SO_4 . After obtaining the CV with characteristic gold peaks the membrane was rinsed thoroughly and used for polymerization. Before starting polymerization the solution was purged with N_2 for half an hour. An EG & G PAR scanning potentiostat (model 362) coupled with a Linseis XYt recorder was used for electropolymerization.

Pore Density Measurement

Pore density of the membrane was measured with the help of scanning electron microscope (JEOL JSM 6400). By measuring the number of pores from the pictures of various regions of the membrane, an average pore density was calculated. The average pore density for 1.2 μm PC membranes was found to be 3.2×10^7 pores cm^{-2} .

In situ Resistance Measurements

During *in situ* resistance measurement, the gold line on one side of the membrane acts as 'source' and that on the opposite side acts as 'drain' of the electrochemical transistor⁶. When a potential difference is applied, current passes through each polymer tubule from one end (source) to the other (drain). Measurements were carried out with the help of a PINE model AFRDE4 bipotentiostat. The resistance of polymer tubule was measured by holding one gold line (one end of the pore) at a potential V_g and the other at $V_g + 20$ mV. The potential difference developed between the electrodes is V_d (20 mV) and the current obtained is designated as I_d . The back ground current I_0 was measured when V_d was 0 mV. The voltage output from the bipotentiostat corresponding to the currents I_0 and I_d , was measured on a Philips 2525 multimeter. The resistance of PPy tubules was calculated by using the expression, $R = V_d / (I_d - I_0)$.

Microscopic Studies

Micrographs were taken using a JEOL JSM 6400 Scanning Electron Microscope (SEM) in the Department of Chemical Engineering, IIT Bombay. Samples were sputter coated with gold to avoid charging. Different acceleration voltages in the range of 5-25 KV were used at a scanning probe current of 1×10^{-10} A to obtain clear images. Formation of PPy on PC surface was observed by pasting the membrane on a metal stub with conducting epoxy paint. PPy tubule formation inside the pores of PC membranes was observed by dissolving the PC membrane in

dichloromethane. In this case, polymer was grown on a single side gold-coated membrane. Sample preparation was done in the following manner. A metal stub was placed in a small beaker containing dichloromethane so that the level of the solvent was just above the stub. A strip of polymer coated PC membrane was slowly introduced into the solvent with the polymer side facing the stub. PC dissolved in solvent leaving behind the polymer which was allowed to sit on the stub by evaporation of solvent. The stub was removed from the beaker and conducting epoxy paint was applied on the edges to fix the polymer film. The whole procedure is schematically represented in Fig. 2, where polymer tubule formation inside the pores of the membrane is shown followed by the procedure of preparing PPy tubule sample for microscopy by dissolving PC membrane.

Electropolymerization Kinetics

Polypyrrole films were electrodeposited on Au-coated PC membranes from an aqueous solution containing 0.1 M pyrrole in presence of 0.1 M KCl. Cyclic voltammograms (CVs) recorded during the formation of a polypyrrole film by cycling the potential between 0.0 to 1.0 V vs. SCE are shown in Fig. 3. In the first cycle, the current starts increasing at 0.7 V and there is a large nucleation loop showing the polymer starts growing on the surface at a significant rate even at low overpotentials once nuclei are formed at high overpotentials. Kinetics of polymerization was studied by chronoamperometry. The chronoamperometric curve was obtained during the potentiostatic electropolymerization of pyrrole. Polymerization was carried out from one side of a 1.2 μm Au-PC membrane from 0.1 M pyrrole in KCl solution by applying a potential-step from 0.0 to 0.6 V vs. SCE. We have observed that polymerization rate depends on the concentration of supporting electrolyte. An increase in

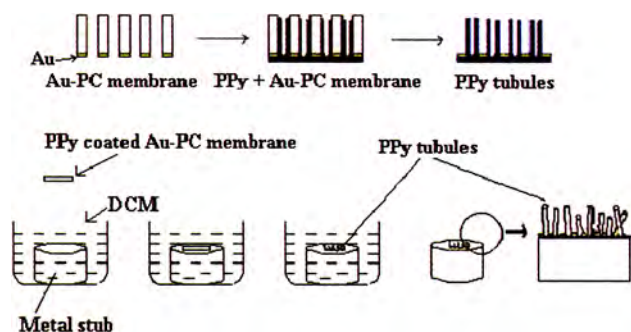


Fig. 2 Schematic diagram showing preparation of PPy tubules for microscopy

polymerization rate with electrolyte concentration has already been reported for the electrosynthesis of conducting polymer films⁸. This phenomenon has been explained in different ways: (a) an increase in conductivity of electrolyte solution, (b) the stabilization of the growing radical cations by the anions of the electrolyte, their coupling being favoured over secondary reaction, and (c) the effect of electrolyte concentration on the formation of oxides on the Pt electrode which catalyze the monomer oxidation^{8d}. Some authors have also suggested that the polymerization process can be initiated by the oxidation of anion⁹. However, the same saturation current was observed irrespective of the used electrolyte concentration. Demoustier-Champagne and Stavaux¹⁰ have shown that the amount of electrodeposited PPy in the pores of polycarbonate track-etched membranes is independent of electrolyte concentration, though the time to obtain completely filled pores varies with the concentration of supporting electrolyte.

The polymeric growth process in the pores of Au-PC membrane can be divided into four different stages. All four steps are clearly observed when polymerization was done at 0.7 V vs. SCE from 0.1 M pyrrole in 0.1 M KCl (Fig. 4). In the same Fig., two pores are drawn schematically in cross section to show the successive

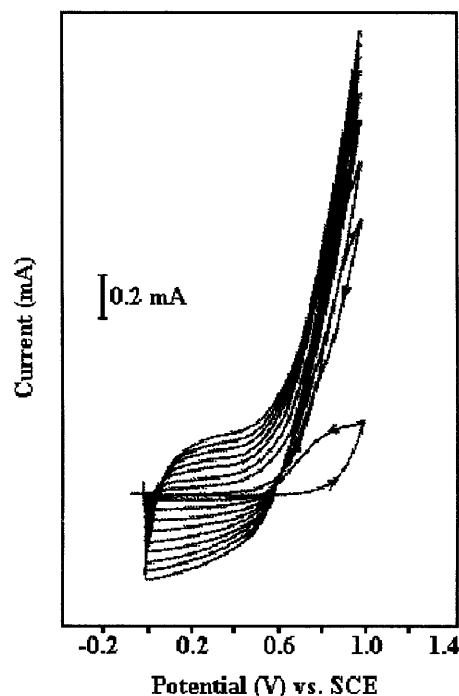


Fig. 3 Electropolymerization of pyrrole on the gold coated PC membrane (1.2 mm) from 0.1 M pyrrole in 0.1 M KCl with a scan rate 50 mV s^{-1}

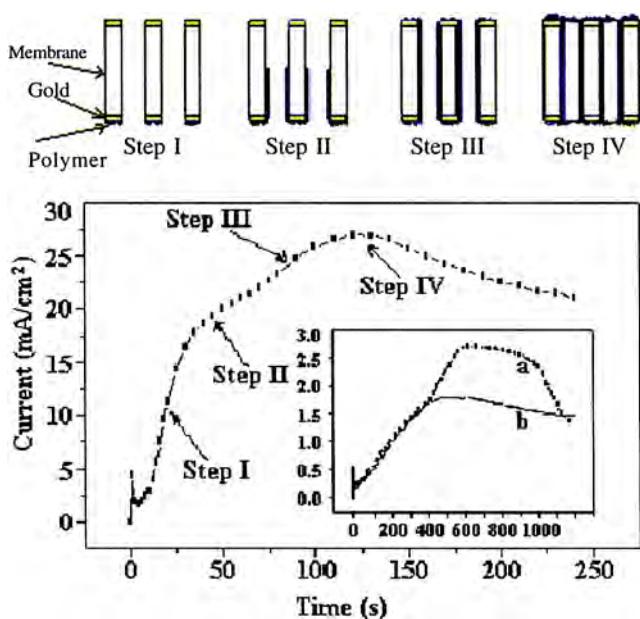


Fig. 4 Chronoamperometric curve for Pyrrole polymerization from one side on a membrane having gold-coating on both the surfaces, in 0.1 M pyrrole at 0.7 V vs. SCE in presence of 0.1 M KCl. The schematic diagram shows the different steps of polymerization as indicated in the Figure. Inset shows the chronoamperograms for pyrrole polymerization from one side at 0.6 V vs SCE : a) on the membrane gold coated on both surfaces, b) on the membrane gold coated on single surface.

stages of the growth process. After a small induction period of ~ 10 sec, current increases rapidly with time (step I) where polymer starts growing on the gold coated membrane surface. The current obtained was linear with time (for ~ 15 sec) indicating that the polymer deposition is proceeding via 2D instantaneous nucleation and growth. After this step, the polymer starts growing through the pores. The polymerization charges calculated for the polymerization upto step I, were similar for different experiments. The calculated charges were in the range of 120 ± 12 mC cm^{-2} irrespective of the potential (0.6 V or 0.7 V vs. SCE) used for the polymerization. This observation indicates almost same amount of polymer formation on the connected gold-coated membrane side, before it grows through the pores. The slope of the chronoamperometric curve changes as the polymer starts growing through pores of the membrane, the corresponding stage is shown as step II. The inflexion of the curve appears, due to the IR drop as the growth proceeds in the pores of the membrane. Further increase of the slope may be explained by the polymer formation on the other surface of the membrane (step III). Once growth proceeds over the opposite surface (step IV) the current shows

a plateau region after which the current fall may be due to IR drop in the thick polymer film. The polymerization reaction may also be limited by the diffusion of pyrrole at this stage. Earlier Demoustier-Champagne and Stavaux¹⁰ have attempted to describe the chronoamperogram obtained for the electropolymerization of pyrrole in pores of PC membrane where one side of the membrane was blocked by a metallic layer. In our case if gold coating was done on single side of the membrane we observed current increasing after a small induction period, there was no inflexion, which can differentiate step II and III (curve b; inset of Fig. 4). After step II there is no further increase in current since there is no gold coating on the opposite side. In this case also we observed current falling after a plateau region and chronoamperogram obtained was similar to that for polymerization on conventional metallic electrode.

To obtain direct evidence of the proposed stages of polymer growth on PC membrane, electron micrographs were taken after various times during the polymerization process. In this set of experiments, the polymerization was done at a potential of 0.6 V vs. SCE. Fig. 5 shows the micrographs of the face of the membrane to which electrical contact with the potentiostat was made (side a) and where polymer growth initiates. Fig. 5 A corresponds to step I, wherein polymer has deposited on the gold surface but the pore mouths are clearly open, even though there is accumulation of polymer globules around the edges of the pore mouth. At longer times (Fig. 5 B), some of the pore mouths are partially blocked, corresponding to step II.

Up to step II we could not see any polymer on the opposite face of the membranes (side b). Figs. 5 C and D show micrographs of the opposite face after 6 min (step II) and 9 min (step III). After 6 min, one can notice polymer deposition around the edges of the pore openings, after 9 min the pore mouth begins to close, and the micrograph shows some completely closed and some partially closed pore openings. Therefore at step III the polymer starts growing on the other side, and before blocking the pores polymer grows on the surface of the opposite side (Fig. 5 D). Fig. 4 E shows the front face after 10 min, by which time a thick film of the polymer has deposited. These observations support the stage-wise growth proposed in Fig. 4.

Microscopic Studies of PPy Tubules Formation

Electropolymerization of pyrrole on Au-PC membrane results in PPy tubules in the pores of PC membranes.

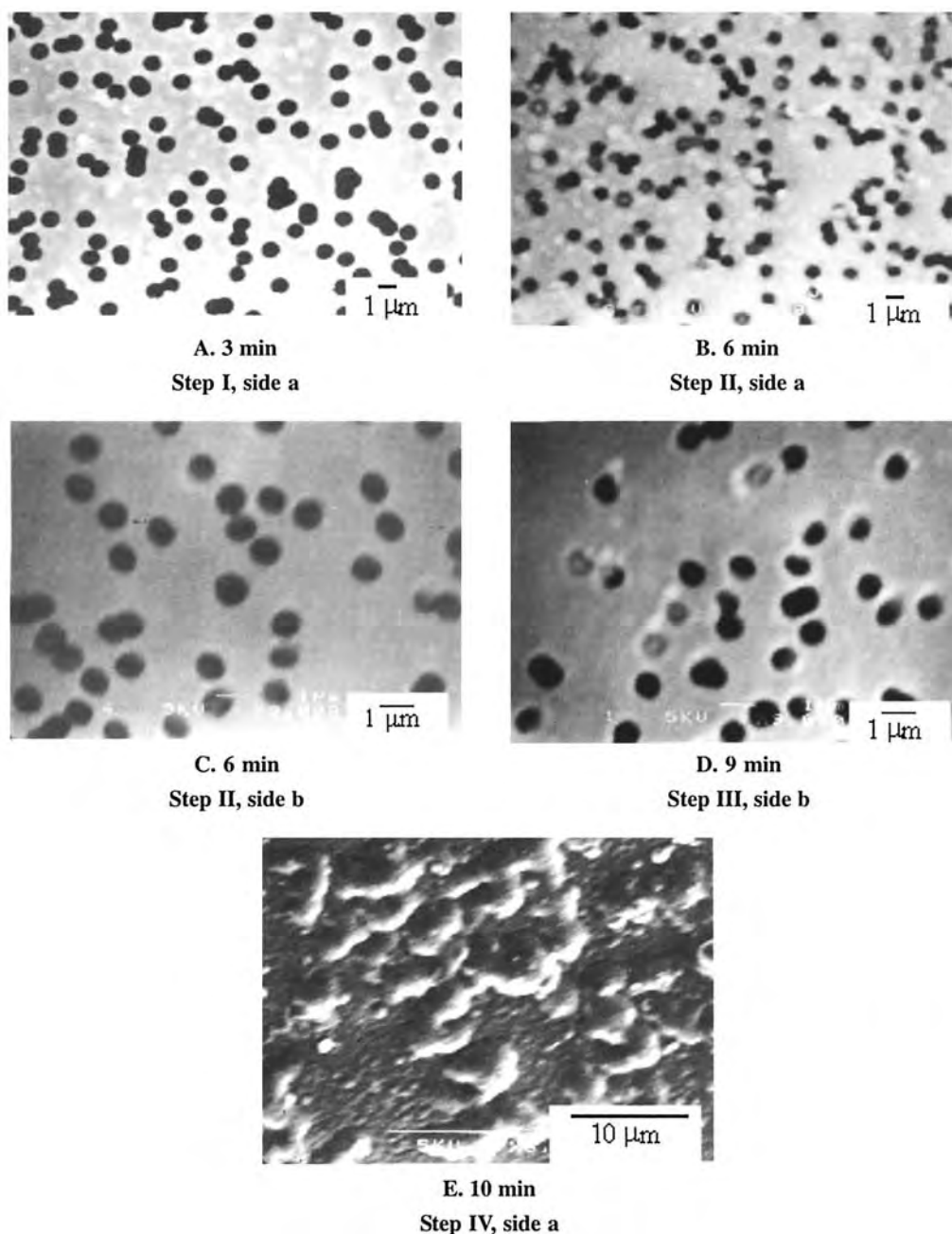


Fig. 5 Micrographs of 1.2 μm PC membrane, A, B and E-for the side connected to potentiostat, (side a), C and D-for the opposite surface (side b) at different electropolymerization steps for potentiostatic polymerization of Py at 0.6 V vs. SCE. Polymerization times are given along with the pictures.

During potentiostatic polymerization at 0.6 V vs. SCE, it was observed that at step III (~ 8 min) polymer appears on the opposite side of the membrane. However in the case of potentiodynamic polymerization (0 to 1.0 V vs. SCE at 50 mV/sec scan rate) it required 6 cycles (~ 4 min) to bridge the membrane pores. Therefore we can expect polymer tubules of $\sim 10 \mu\text{m}$ length (i.e. the thickness of the membrane) when polymerization was done for longer times than is required to bridge the

membrane pores. By dissolving PC membrane in dichloromethane the polymer tubules were observed under SEM. PPy tubules formed by potentiodynamic polymerization for 6, 10 and 30 minutes are shown in Fig. 6. We observed tubules of $\sim 10 \mu\text{m}$ length in all these cases. Tubules formed for 10 min (Fig. 6 A) are slightly thicker than the case where 6 min electropolymerization (Fig. 6 B) was done. The morphology of the polymers on the membrane surface (connected to the potentiostat)

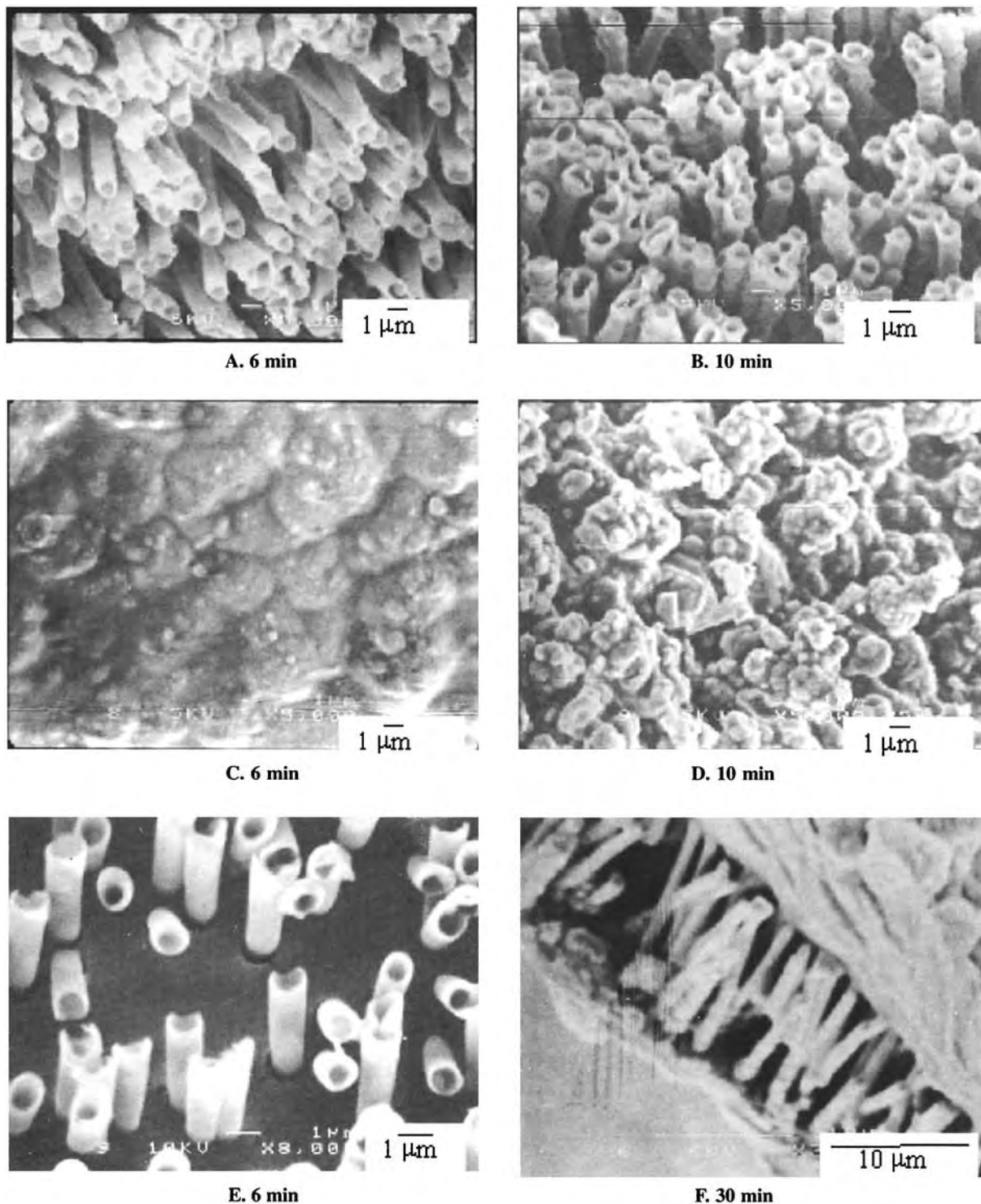


Fig. 6 Micrographs of PPy tubules at different polymerization times. (A). Tubules after 6 min electropolymerization by potentiodynamic method. (B) Tubules after 10 min electropolymerization by potentiodynamic method, the tubules are thicker than the case A. (C) Surface morphology of case A. (D). Surface morphology of case B, thick PPy film showing a morphology like cauliflower. (E) PPy tubules after 6 min potentiodynamic electropolymerization with the base of gold layer below which there will be polymer film. (F) Micrographs of PPy tubules after 30 min potentiodynamic electropolymerization connecting one side of the membrane. Polymer has been formed on the other side of the membrane, which was not connected. PPy films on both the side holding the tubules of $\sim 10 \mu\text{m}$ length.

are also shown in the same Figs. 6 C and 6 D. It is obvious that long time polymerization results in big globules on the surface. Fig. 6 E shows magnified PPy tubules with its gold-polymer base. In this case polymerization was done for 6 min. We could clearly observe the almost parallel PPy tubules. Longer polymerization time (30 min) results in a PPy layer on the opposite side of the membrane also. Fig. 6 F shows PPy tubules with PPy films on both sides, the tubules, which are much thicker than the other two cases holding the two PPy films 10 μm apart.

In situ Resistance Measurement in 0.1 M KCl Solution

Resistance of the PPy tubules formed in the pores of Au-PC membrane depends on the polymerization time, diameter of the pores and on the length of the pores (thickness of the membrane). The resistance of a single tubule of PPy (R_{pore}) can be calculated from the resistance of the PPy film (R_{T}) measured. As the tubules are aligned parallel to each other they can be considered as a set of parallel resistors.

$$\frac{1}{R_{\text{T}}} = \sum_1^n \frac{1}{R_{\text{pore}}} = \frac{n}{R_{\text{pore}}}$$

$$R_{\text{pore}} = nR_{\text{T}}$$

where n is the total number of pores, which can be calculated from the pore density and the area of the film used. Fig. 7 shows the change of R_{pore} with the potential. Polymer was obtained by potentiodynamic polymerization for 8 min. The resistance of a single PPy tubule is high at higher negative potentials ($7.86 \times 10^9 \Omega$ at -1.0 V vs. SCE), and decreases with increasing potential ($1.63 \times 10^7 \Omega$ at 0.6 V vs. SCE). However, after $+0.6 \text{ V vs. SCE}$ an increase in resistance was observed which is due to the overoxidation of the polymer.

Fig. 8 shows the change of R_{pore} with the polymerization time; after 3 min of potentiostatic polymerization there was no connection between the two side of the membrane. After 6 min, we observed that the resistance started decreasing indicating some of the pores started connecting the two sides by polymer. After 10-minute electropolymerization almost all the pores connect the two side of the membrane by polymer tubules. With increasing polymerization time, tubules become thicker and the resistance of the tubule (R_{pore}) decreases with polymerization time. However, this change is not uniform at all potentials. At a negative potential, the change is larger where the polymer acts

as an insulator (Fig. 9). When there is no further decrease in R_{pore} we can assume that the pores are now completely plugged. For potentiodynamic polymerization, completely plugged pores were obtained within 15-17 minutes (Fig. 9). We have observed similar type of dependence of R_{pore} with electropolymerization time for potentiostatic case also. After obtaining completely plugged pores the change of conductance with potential are similar for both the cases. The values of R_{pore} obtained at this stage are $4.2 \times 10^7 \Omega$ at -0.5 V vs. SCE and $3.72 \times 10^6 \Omega$ at 0.5 V vs. SCE .

A number of similar experiments with PPy coated PC membrane, were carried out under identical condition. Table I shows the value of R_{pore} at -1.0 and $+0.5 \text{ V vs. SCE}$, obtained for completely plugged PPy in the tubules of $1.2 \mu\text{m}$ PC membrane in the solution of 0.1 M KCl . Switching factor i.e the ratio of the

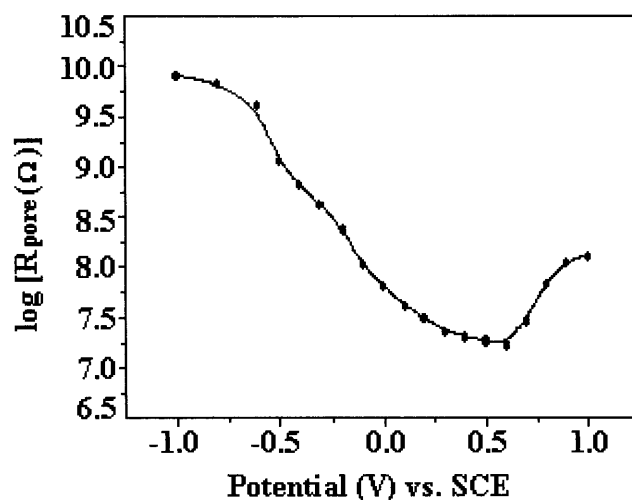


Fig. 7 Plot of $\log (R_{\text{pore}})$ vs. potential for PPy tubules ($1.2 \mu\text{m}$) after potentiodynamic polymerization of 8 min.

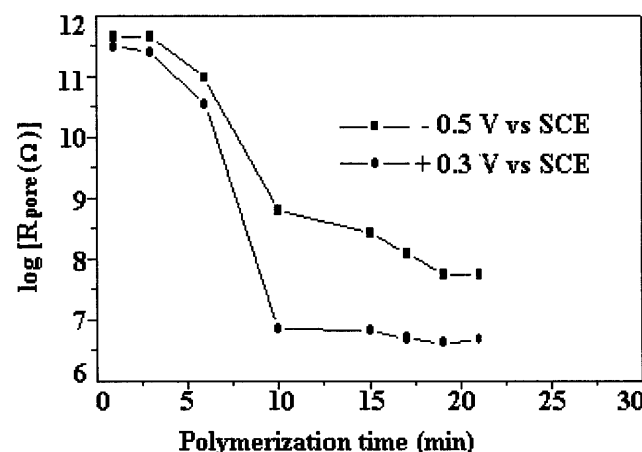


Fig. 8 Plots of $\log (R_{\text{pore}})$ vs. potentiostatic polymerization time for pyrrole.

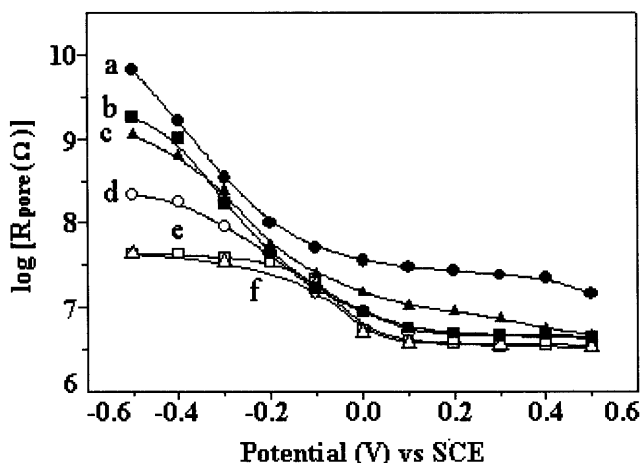


Fig. 9 Plots of $\log(R_{\text{pore}})$ vs. potential for PPy tubule at different potentiodynamic electropolymerization time. (a) 3, (b) 5, (c) 6, (d) 12, (e) 17 and (f) 21 min.

Table I

The values of R_{pore} at -1.0 and $+0.5$ V vs. SCE, and the switching factor, i.e. the ratio of the resistances in the conducting to that in the insulating state for PPy tubules ($1.2 \mu\text{m}$). Mean and standard deviation (S.D) are also given

S. No.	At -1.0 V vs. SCE (Ω)	At $+0.5$ V vs. SCE (Ω)	Switching Factor
1.	0.66×10^{10}	1.75×10^7	3.77×10^2
2.	1.11×10^{10}	2.32×10^7	4.78×10^2
3.	0.59×10^{10}	1.16×10^7	5.08×10^2
4.	1.11×10^{10}	2.77×10^7	4.00×10^2
5.	0.83×10^{10}	1.82×10^7	4.56×10^2
6.	0.37×10^{10}	1.39×10^7	2.66×10^2
Mean	0.77×10^{10}	1.86×10^7	4.14×10^2
S. D	0.27×10^{10}	0.54×10^7	0.79×10^2

resistances in the conducting to that in the insulating state for PPy at pH ~ 6 is 415.

From the resistance of the completely plugged PPy tubule (R_p) we can calculate the conductivity (σ) for PPy.

$$R_p = \rho \frac{\ell}{A} \text{ and } \sigma = \frac{1}{\rho} = \frac{1}{AR_p}$$

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where ρ is the resistivity, ℓ is length ($10 \mu\text{m}$) of the pore, A is area of the pore [$\pi (1.2/2)^2 \mu\text{m}^2$]. The minimum conductivity at -1.0 V vs. SCE (in 0.1 M KCl solution), obtained was $1.31 \times 10^{-5} \text{ S cm}^{-1}$ while the maximum conductivity at $+0.5$ V vs. SCE obtained was $5.15 \times 10^{-3} \text{ S cm}^{-1}$. Wang *et al.*¹¹ have shown similar type of dependence of conductivity with potential using platinum dual-disk microelectrode. They have prepared PPy by cycling the potential between -0.8 to $+0.8$ V vs. SCE. For their case the maximum conductivity obtained at $+0.5$ V vs. SCE is $1.25 \times 10^{-3} \text{ S cm}^{-1}$ and in the reduced state the conductivity is $8.4 \times 10^{-5} \text{ S cm}^{-1}$. However, the oxidized film conductivity is significantly lower than the literature value for dry state oxidized PPy, $40\text{--}100 \text{ S cm}^{-1}$. The reason for lower conductivity is not clear, it may be the effect of the chemical potential of the microenvironment, or the films as we grow them may be less morphologically compact.

Conclusions

The chronoamperograms obtained for electropolymerization on the porous membrane have been explained in detail. The polymerization current vs polymerization time plot for electropolymerization on a membrane having gold coating on both faces is different from that for electropolymerization on a single side coated membrane. In the former case four steps of electropolymerization has been elucidated with the help of SEM pictures of the membrane surface at different electropolymerization times. Characterization of the PPy microtubules was done by *in-situ* conductance measurements. The polymer matrix inside the pores of the membrane shows a two order change in conductance on changing from oxidized to reduced state.

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