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**SYNTHESIS OF CONDUCTING POLYMER COMPOSITE FIBERS  
IN ELECTROCHEMICAL FLOW CELLS**

by

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# Synthesis of Conducting Polymer Composite Fibers in Electrochemical Flow Cells

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**Abstract.** A one-step electrochemical synthesis of polymer and composite polymer fibers of macroscopic dimensions (>10 cm length and 0.2 mm diameter) is reported. Poly(3-methylthiophene) and polypyrrole fibers are grown from the tip of a Pt microelectrode by oxidation of 3-methylthiophene and pyrrole, respectively, in a capillary flow cell. Hydrodynamic fields within the capillary cell result in unidirectional growth of the polymer along the axis of the flow cell. High strength, conductive, and flexible composite polymer fibers are synthesized by deposition of poly(3-methylthiophene) or polypyrrole on a non-conductive Kevlar or polyester string suspended in the solution along the axis of the capillary flow cell. Composite fiber growth rates as large as 30 cm/hr are obtained under optimal conditions.

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**Introduction.** An earlier report from this laboratory described the electrochemical synthesis of conducting polymer fibers of macroscopic dimensions[1]. Specifically, fibers of poly(3-methylthiophene), abbreviated hereafter as poly(3-MT), of length greater than 10 cm and diameter between 0.1 and 0.7 mm were grown from the tip of a platinum electrode by galvanic oxidation of 3-MT in a capillary flow cell. Within a narrow window of



experimental conditions, which are defined by the flow velocity, applied current, and 3-MT concentration, polymer fibers were obtained at a linear growth rate of  $\sim 1$  cm/hr and at  $\sim 80\%$  current efficiency. In contrast, oxidation of 3-MT in stagnant solutions, or at rotating disk electrodes[2], resulted in the deposition of a thin film ( $\leq 1 \mu\text{m}$ ) on the electrode surface. The dependence of the shape of the fiber and the rate of fiber growth on the electrochemical and flow parameters indicated that coupling of hydrodynamic forces in the flow cell, with the chemical kinetics of monomer oxidation and oligomer deposition, defines the necessary conditions for fiber growth [1].

In the present report, we describe related investigations concerning the synthesis of composite polymer fibers comprised of either poly(3-MT) or polypyrrole [3,4,5,6] and nonconductive Kevlar or polyester strings. In contrast to the single-phase poly(3-MT) fibers, which are extremely brittle and mechanically weak, the composite fibers exhibit excellent mechanical properties, while maintaining the electrical conductivity and electrochemical properties associated with thin films of poly(3-MT) or polypyrrole. In addition to this improvement of the materials properties, the methodology we have developed for preparing composite fibers also provided a 30-fold increase in the fiber growth rate.

**Experimental.** Poly(3-MT), polypyrrole, and composite fibers were grown under galvanostatic control in the flow cells shown in Fig. 1a and b. Construction of the cells have been described previously [1,7]. The anode and cathode were platinum wires with diameters of 127  $\mu\text{m}$  and 1 mm, respectively. The flow cells were oriented vertically on the lab bench, and solutions containing the monomer and a supporting electrolyte were pumped into the cell through the entrance port near the anode. Volumetric flow rates were varied between 10 and 50 ml/s using a centrifugal pump (Cole - Parmer, model 07002 - 60). The Pt anode was encapsulated in glass with  $\sim 1$  cm of the wire extending past the end of the glass insulation. This electrode was positioned in the center of the capillary,  $\sim 5$  cm from the entrance port.

The flow cell shown in Fig. 1a was used to grow single-phase polymer fibers in solutions containing either 3-MT or pyrrole and a supporting electrolyte. Oxidation of pyrrole or 3-MT at the Pt anode in the cell shown in Fig. 1a resulted in growth of a single fiber attached to the end of the electrode. In other experiments, a non-conductive Kevlar or polyester string was placed in the center of the capillary cell by attaching one end of the string to the end of the Pt anode and the other end to the stopper near the exit port, Fig. 1b. The non-conductive strings were attached to the tip of the Pt anode using a non-conductive epoxy (Epoxy-Patch, Dexter). Oxidation of the monomer at the anode resulted in growth of the polymer onto and along the non-conductive fiber.

The conductivity of the fibers was measured using the 4-point probe method. Electrical contacts to the polymer fiber were made using silver epoxy. Scanning electron microscope images were obtained using a JEOL II 840 electron microscope operating at 10 kV. Cyclic voltammetry was performed using a EG&G PAR model 173 potentiostat and model 175 programmer.

3-MT, pyrrole, sodium polystyrenesulfonate ( $\text{Na}^+\text{PSS}^-$ ), sodium dodecylbenzenesulfonate ( $\text{Na}^+\text{DBS}^-$ ), tetrabutylammonium p-toluenesulfonate ( $\text{TBA}^+\text{TS}^-$ ) and sodium polyvinylsulfonate ( $\text{Na}^+\text{PVS}^-$ ) were purchased from Aldrich and used as

received. Bis(triphenylphosphoanylidene)ammonium polystyrenesulfonate (PPN<sup>+</sup>PSS<sup>-</sup>) was prepared by metathesis of Na<sup>+</sup>PSS<sup>-</sup> and PPN<sup>+</sup>Cl<sup>-</sup> (Aldrich), washed with deionized water and dried under vacuum. Kevlar (Goodfellow Co., 70 filaments with a filament diameter of 0.0167mm) and polyester strings (0.1 mm diameter) were used without pretreatment.

## Results.

*Polypyrrole and Poly(3-MT) Fibers.* We previously reported that 10 cm long poly(3-MT) fibers can be grown in the electrochemical flow cell shown in Fig. 1a from an acetonitrile (CH<sub>3</sub>CN) solution containing 0.5 M 3-MT and 0.1 M TBAP [1]. 3-MT is oxidized at the upper Pt wire by passing an anodic current (typically 1-3 mA) through this electrode. Initially, a thin film of poly(3-MT) is deposited uniformly over the surface of the electrode. Continued oxidation of 3-MT at constant current results in the growth of a single fiber of uniform diameter from the Pt anode. In all experiments, the fiber grows along the axial center of the flow capillary without touching the capillary walls. An optical photograph of a poly(3-MT) fiber grown at 1.8 mA and a flow rate of 30 cm/s is shown in Fig. 2. Depending on the flow velocity and applied current, the growth rate of poly(3-MT) fibers varied from 0.2-3 cm/hr. (All flow velocities reported herein are average velocities calculated from the volumetric flow rate and capillary diameter).

The poly(3-MT) fibers obtained from CH<sub>3</sub>CN/TBAP solutions are very fragile and break easily when handled. In order to improve their mechanical properties, we attempted to incorporate polystyrenesulfonate (PSS<sup>-</sup>) into the fiber during growth by replacing the supporting electrolyte, TBAP, with PPN<sup>+</sup>PSS<sup>-</sup> [8,9,10,11]. However, we were not able to obtain a fiber in the presence of PPN<sup>+</sup>PSS<sup>-</sup> under similar conditions used to grow poly(3-MT) fibers from CH<sub>3</sub>CN/TBAP solutions.

In contrast to results obtained for the growth of poly(3-MT) fibers, we have been unable to grow polypyrrole fibers from oxidation of pyrrole ( $x$  pyrrole  $\rightarrow$  polypyrrole +

$2xe^- + 2xH^+$ ) in  $CH_3CN/TBAP$  solutions. However, polypyrrole fibers of macroscopic dimensions can be readily synthesized in an aqueous solutions containing  $Na^+PSS^-$  as the supporting electrolyte. An optical photograph of a typical polypyrrole( $PSS^-$ ) fiber, grown at a current of 1 mA and a flow rate of 15 cm/s in an aqueous 1%  $Na^+PSS^-$  solution, is shown in Fig. 2. As with the growth of poly(3-MT) fibers [5], the deposition of polypyrrole occurs at the end of the growing fiber, resulting in a fiber of uniform diameter. However, for the same applied current, polypyrrole fibers tend to grow at lower linear growth rates but with larger diameters than poly(3-MT) fibers. For example, at a flow velocity of 20 cm/s and an applied current of 1 mA, a polypyrrole fiber grew at  $\sim 0.14$  cm/hr with a diameter of 1.1 mm, while a poly(3-MT) fiber grew at  $\sim 0.82$  cm/hr with a diameter of 0.55 mm. We have not been successful in growing polypyrrole fibers in  $CH_3CN$  solutions containing either  $TBA^+TS^-$  or  $PPN^+PSS^-$  as the supporting electrolyte, or in aqueous solutions containing  $Na^+DBS^-$ ,  $Na^+PVS^-$  or  $Na^+TS^-$ . The strong dependence of the conditions necessary for polymer growth on the nature of the supporting electrolyte is not understood.

The growth rate and diameter of the polypyrrole ( $PPS^-$ ) fibers depended on several experimental parameters, including faradaic current, supporting electrolyte concentration and flow rate. Fibers of uniform diameter (0.5 - 2.0 mm) were grown at low flow velocities (10 - 35 cm/s). At higher flow velocities (50 cm/s), a short cone-shaped polypyrrole fiber was obtained at the tip of the electrode. Larger currents typically resulted in faster growth rates and larger diameters. Under otherwise identical conditions, polypyrrole fibers grown at a higher  $Na^+PPS^-$  concentration (5%) have larger diameters than those grown at a lower supporting electrolyte concentration (0.5%).

The electrical conductivity of a 2 mm diameter, 4 cm long polypyrrole ( $PPS^-$ ) fiber was measured to be  $6.2 \Omega^{-1} cm^{-1}$ , in good agreement with the conductivity of polypyrrole films prepared in a stagnant solution [4 (b), (c)]. Similarly, the infrared absorption

spectrum of a polypyrrole( $\text{PPS}^-$ ) fiber was essentially identical to that of a polypyrrole( $\text{PPS}^-$ ) film prepared in a stagnant solution.

*Composite Fibers.* Polypyrrole ( $\text{PPS}^-$ ) fibers are significantly harder and stronger than poly(3-MT) fibers. However, both materials are brittle and break when flexed. To improve the flexibility of these materials, we used the following approach to synthesize composite polymer fibers in the electrochemical flow cell shown in Fig. 1b.

A 10 cm-long Kevlar or polyester string was positioned at the center of the capillary cell. One end of the string was attached to the Pt wire anode with a nonconductive epoxy, as shown in Fig. 1b. When a constant current of 1 mA to 3 mA was applied to the electrode with a solution of 3-MT or pyrrole flowing through the cell, a uniform polymer film deposited on the Pt electrode. With continued oxidation of the monomer, the film then grew onto the non-conductive string, rapidly coating the entire length of the string (up to 10 cm in length).

Poly(3-MT) and polypyrrole were grown on polyester strings in an  $\text{CH}_3\text{CN}$  solution containing TBAP. The polypyrrole films adhered extremely well to the polyester string, while poly(3-MT) could be easily removed by gently rubbing the string. Thus, we limited our study to the growth of polypyrrole composites. Polyester/polypyrrole and Kevlar/polypyrrole composite fibers were successfully grown in  $\text{CH}_3\text{CN}$  and in aqueous solutions containing a number of different supporting electrolytes ( $\text{TBA}^+\text{TS}^-$ ,  $\text{Na}^+\text{PSS}^-$ ,  $\text{Na}^+\text{DBS}^-$ ,  $\text{Na}^+\text{PVS}^-$ , and  $\text{Na}^+\text{TS}^-$ ). Photographs of polyester/polypyrrole and Kevlar/polypyrrole composite fibers are shown in Fig. 3. SEM images of the composite fibers show that polypyrrole deposits uniformly between the filaments of the nonconductive strings, as well as on the outside surface of the strings. Figs. 4 and 5 show SEM images of Kevlar/polypyrrole fibers grown from  $\text{CH}_3\text{CN}/\text{TBA}^+\text{TS}^-$  and  $\text{H}_2\text{O}/\text{Na}^+\text{DBS}^-$  solutions.

The flexibility of the resulting composite was qualitatively tested by making a 180° bend in the string, and examining the string for cracks under an optical microscope. Composite fibers obtained from CH<sub>3</sub>CN/TBA<sup>+</sup>TS<sup>-</sup> solutions using Kevlar strings could be repeatedly flexed without any noticeable cracking. Images of the cross-section morphology of Kevlar/polypyrrole fibers prepared using TBA<sup>+</sup>TS<sup>-</sup> as supporting electrolyte (Fig. 4a) show that the polymer phase undergoes plastic deformation when the fiber is cut with a razor blade, consistent with excellent flexibility of the fiber. Other fibers, including the Kevlar/polypyrrole composite fiber prepared from aqueous Na<sup>+</sup>DBS<sup>-</sup> solution and shown in Fig. 5b, display smoother and sharper cross sections, indicative of brittle fracture. Table I summarizes the results from our bending tests and the electrical conductivity of several polypyrrole composites fibers.

The linear growth rate of the polypyrrole composite fibers depended strongly on the the electrolyte composition and could be varied by one order of magnitude for different solvent/electrolyte combinations. The largest fiber growth rates were obtained in CH<sub>3</sub>CN solutions containing 0.1 M TBA<sup>+</sup>TS<sup>-</sup>. In this solution, linear growth rates of 30 cm/hr at an applied current of 3 mA and flow rate of 20 cm/s were obtained for the deposition of polypyrrole on Kevlar. The growth rate of the polypyrrole composites did not strongly depend on the type of nonconductive string or on the solution flow rate; however, smoother fiber surfaces were obtained at higher solution flow rates.

## Discussion.

We previously proposed that growth of single-phase poly(3-MT) fibers results from a decrease in the rate of 3-MT oxidation and/or oligomer deposition along the sides of the fiber, relative to that at the growing tip [1]. Furthermore, since the polymer fibers grow only along the axis of the flow cell, it is clear that hydrodynamic flow patterns in the cell are coupled with the kinetics of the oligomer deposition and fiber growth. The ability to synthesize polypyrrole fibers indicates that these phenomena are general and not specific

to the chemistry of 3-MT. However, the strong dependence of fiber growth on the nature of the supporting electrolyte clearly suggests that molecular interactions have a more pronounced effect on the nucleation and growth of the fibers than previously anticipated.

The mechanism of growth of the polymer composite fibers appears analogous to the mechanism previously describe for growth of single-phase fibers; electrical conduction in the fiber allows current to flow to the end of the polymer composite phase, where 3-MT (or pyrrole) is oxidized and deposited at the interface between the nonconductive string and the polymer composite. As with the single-phase fibers, the fact that the composite fibers have a uniform diameter over lengths of 1 to 10 cm suggests that the rate of polymer deposition is significantly larger at the end of the composite polymer phase than along the sides of the composite fiber.

The order of magnitude increase in fiber growth rates obtained by depositing pyrrole and 3-MT on nonconductive strings is not understood. A number of factors could be responsible for this enhancement, including the possibility that the filaments of the nonconductive string behave as nucleation sites for the deposition of the conductive polymer. In addition to coating the exterior surface of the string, SEM images show that poly(3-MT) and polypyrrole are deposited within the bundle of filaments that make up the string. However, we have not observed significant thickening of the exterior conductive polymer phase; i.e, the diameter of the composite fiber has essentially the same value as that of the nonconductive string from which it is fabricated. This finding again suggests that the rate of polymer growth along the fiber surface is relatively slow in comparison to that at the end of the polymer composite phase. The general phenomenon of electrochemical deposition of a conductive material on a nonconductive substrate is currently under study in our laboratory.

The composite fibers have significantly improved properties relative to the single-phase poly(3-MT) or polypyrrole fibers. In addition to the demonstrated improvement in the flexibility and strength, and the strong adhesion between the nonconductive and

conductive phases, the Kevlar/pyrrole fibers are electroactive and can be used as free standing electrodes. For example, Fig. 6a shows the voltammetric response of a 0.7 cm long, 0.2 mm diameter Kevlar/polypyrrole fiber in an aqueous 0.1 M Na<sup>+</sup>TS<sup>-</sup> solution. Although ohmic distortion of the voltammetric waves produces a large separation between the anodic and cathodic peaks as compared to the voltammogram of the corresponding thin film (Fig. 6b), the steady-state voltammetric response qualitatively demonstrates that the fiber undergoes a chemically reversible oxidation and re-reduction. The voltammetric wave is centered at ~ -0.4 V (vs. SCE), in reasonable agreement with the redox potentials reported for thin polypyrrole films in aqueous solutions.

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Table I. Conductivity and Flexibility of Polypyrrole Composite Fibers

	<u>Conductivity</u> $\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	<u>Flexibility</u>
Polyester H <sub>2</sub> O/Na <sup>+</sup> PSS <sup>-</sup>	4.1	Poor
Polyester CH <sub>3</sub> CN/TBAP	4.1	Poor
Kevlar H <sub>2</sub> O/Na <sup>+</sup> DBS <sup>-</sup>	5.4	Poor
Kevlar CH <sub>3</sub> CN/TBA <sup>+</sup> TS <sup>-</sup>	24.3	Good

## Figure Captions

- Figure 1 Schematic drawing of the electrochemical flow cells used to grow: (a) conducting polymer fibers and (b) composite polymer fibers.
- Figure 2 Photographs of a poly(3-MT) fiber prepared in an  $\text{CH}_3\text{CN}$  solution containing 0.5M 3-MT and 0.1M TBAP, and a polypyrrole fiber prepared in an aqueous solution containing 0.5M pyrrole and 1%  $\text{Na}^+\text{PSS}^-$ .
- Figure 3 Photograph of: (a) a polyester/polypyrrole and (b) Kevlar/polypyrrole composite fibers prepared in  $\text{CH}_3\text{CN}$  containing 0.1M TBAP and 0.5M pyrrole.
- Figure 4 SEM images of the (a) side and (b) cross-section of a Kevlar/polypyrrole composite fiber prepared in  $\text{CH}_3\text{CN}$  containing 0.5M pyrrole and 0.1  $\text{TBA}^+\text{TS}^-$ .
- Figure 5 SEM images of the (a) side and (b) cross section of a Kevlar/polypyrrole composite fiber prepared in an aqueous solution containing 0.5M pyrrole and 0.1M  $\text{Na}^+\text{DBS}^-$ .
- Figure 6 Cyclic voltammetric responses of: (a) a 0.7 cm long, 0.2 mm diameter Kevlar/polypyrrole composite fiber electrode; and (b) a 1 cm long 127  $\mu\text{m}$  diameter Pt wire coated with a polypyrrole thin film. Both electrodes were immersed in an aqueous 0.1 M NaTS solution and scanned at a rate of 50 mV/s. The composite fiber and film were grown in an  $\text{CH}_3\text{CN}$  solution containing 0.1M  $\text{TBA}^+\text{TS}^-$  and 0.5 M pyrrole.

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## References

1. S. Li, C. W. Macosko and H. S. White, *Science*, **259**, 957 (1993).
2. P. Lang, F. Chao, M. Costa and F. Garnier, *Polymer*, **28**, 668 (1987).
3. L. P. Rector, D. C. De Groot, J. L. Schindler, T. J. Marks, S. H. Carr, *Synth. Met.*, **41 - 43**, 935 (1991).
4. H. Nemoto, T. J. Marks, D. C. De Groot, C. R. Kannewurf, *Synth. Met.*, **41 - 43**, 415 (1991).
5. S. E. Lindsey, G. B. Street, *Synth. Met.*, **10**, 67 (1984/85).
6. M. De Paoli, R. J. Waltman, A. F. Diaz, J. Bargon, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1687 (1985).
7. D. J. Earl, H. J. Kragt, C. W. Macosko and H. S. White, *Ind. Eng. Chem. Res.*, **30**(1), 264 (1991).
8. J. R. Reynolds, M. B. Gieselman, Y. J. Qiu, M. H. Pyo, *Polym. Mater. Sci. & Eng.*, **64**, 202 (1991).
9. L. F. Warren, D. P. Anderson, *J. Electrochem. Soc.*, **134**, 101 (1987).
10. U. G. Wettermark, G. A. Worrell, C. S. Chen, M. B. Gieselman, J. R. Reynolds, *Polym. Mater. Sci. & Eng.*, **64**, 267 (1991).
11. M. B. Gieselman, J. R. Reynolds, *Macromolecules*, **23**, 3118 (1990).

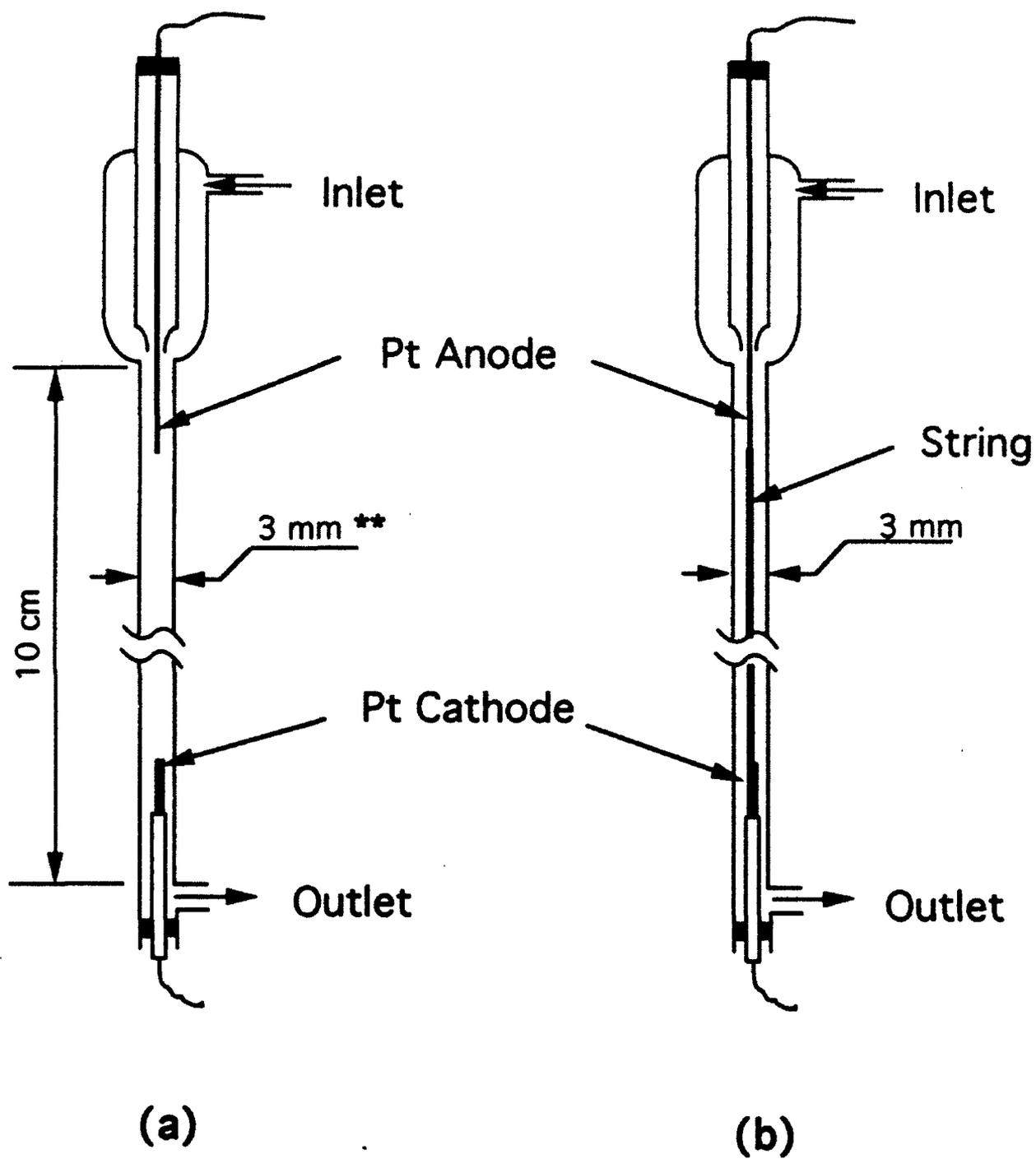


Fig 1

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P(3-MT)

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PPY



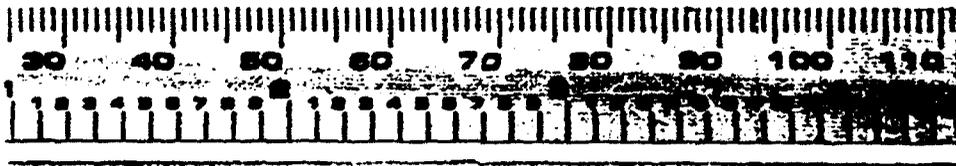
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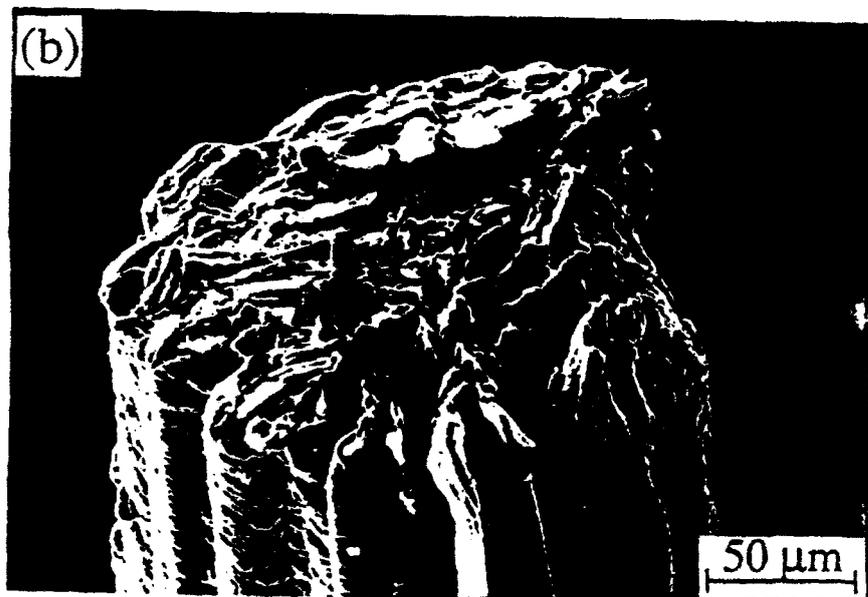
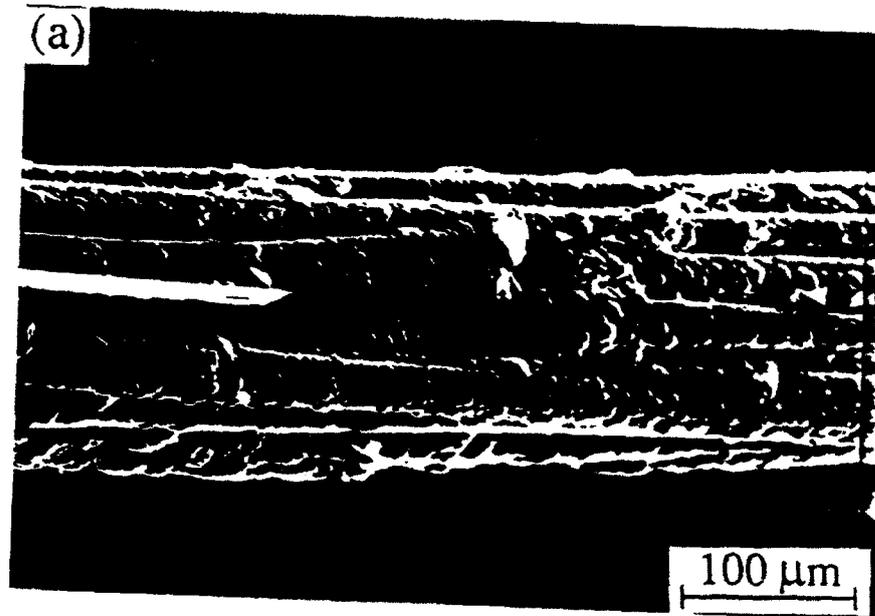
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(a)

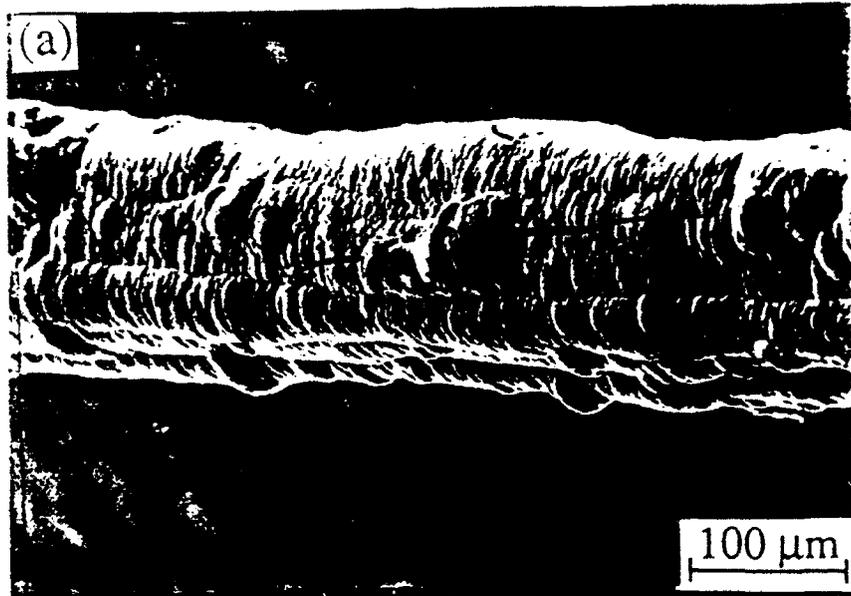
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(b)





F-4



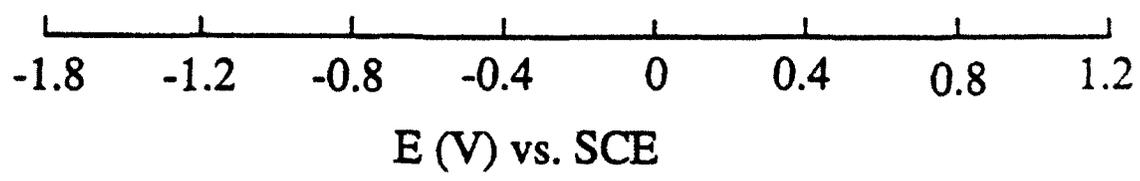
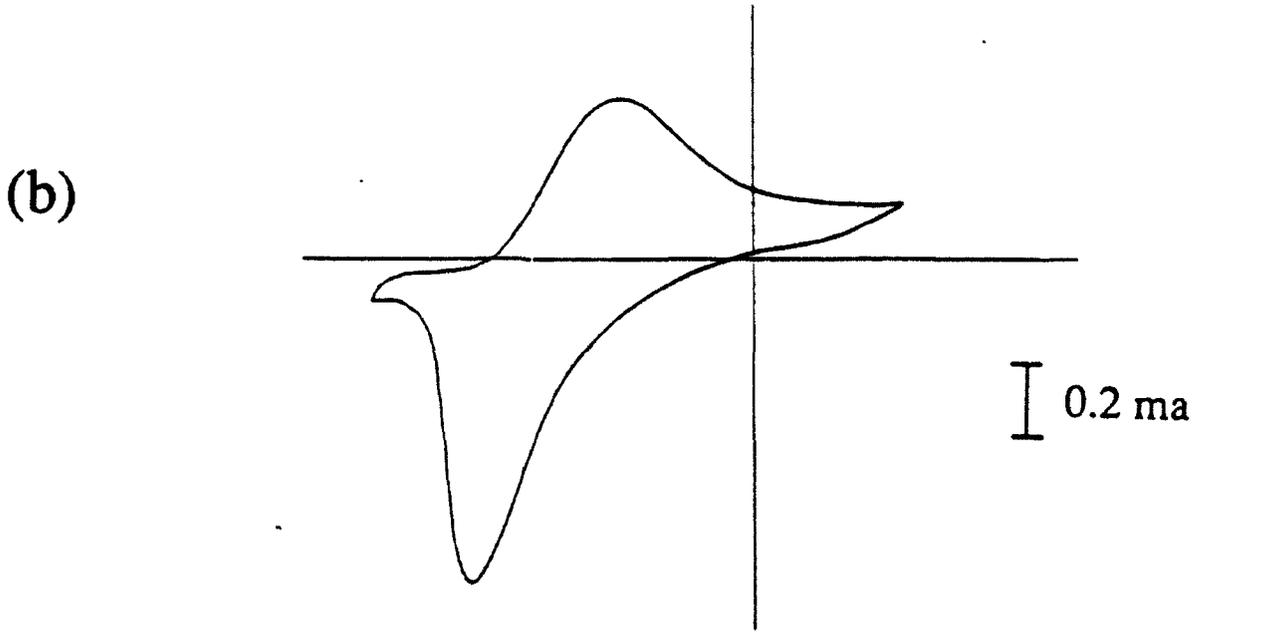
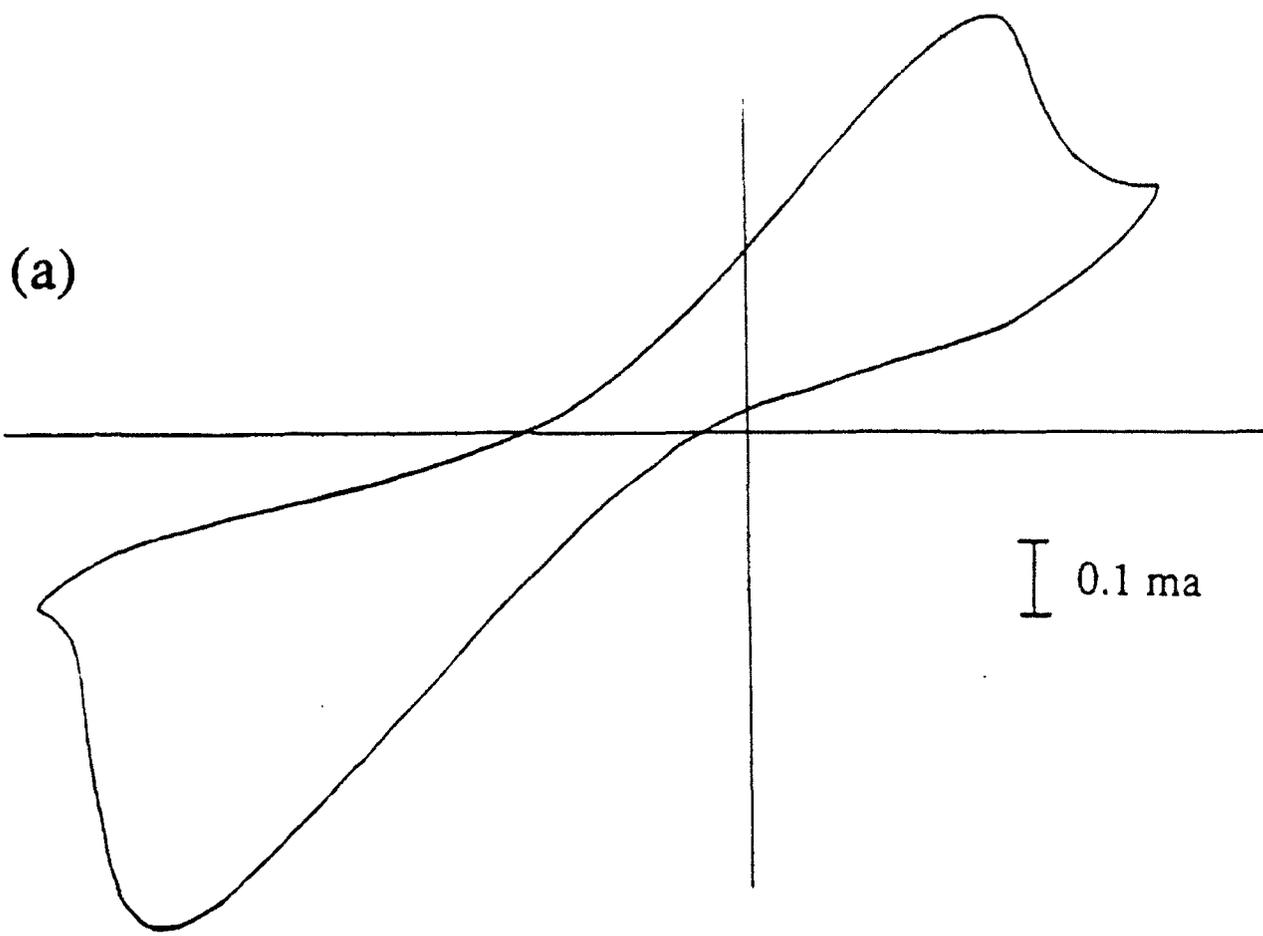


Fig 6