containing ~4.5 mol % dissolved Y_2O_3 and solid Y_2O_3.

Summary

The Gibbs energy of formation of $CuYO_2$ from component oxides has been determined by electrochemical measurements for the first time. Previous measurements on the Gibbs energy of formation of $Cu_2Y_2O_5$[5,6] were based on the coexistence of this compound with Cu_2O and Y_2O_3, ignoring the presence of $CuYO_2$. Although the phases $Cu_2O + Y_2O_3 + Cu_2Y_2O_5$ are not in stable equilibrium, they can coexist metastably due to the slow rate of formation of $CuYO_2$ from Cu_2O and Y_2O_3. The use of stable equilibrium phase assemblages in the present study gives values for the Gibbs energy of formation of $Cu_2Y_2O_5$ from component oxides in reasonable agreement with earlier measurements,[5,6] which were inadvertently based on metastable conditions. Ternary phase diagram of the system Cu–Y–O at 723, 950, and 1373 K have been composed by using thermodynamic data obtained in this study and auxiliary information from the literature. The isobaric section at $P_{O_2} = 2.1 \times 10^4$ Pa has also been constructed.

Registry No. $CuYO_2$, 87588-40-7; $Cu_2Y_2O_5$, 12158-85-9; Cu, 7440-50-8; Y, 7440-65-5; O_2, 7782-44-7; Y_2O_3, 1314-36-9.

Morphological Control of Electropolymerization on Porous Substrates

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Unique morphologies are achieved when pyrrole and 3-methylthiophene are electrochemically polymerized on two porous substrates, Nuclepore and stainless steel mesh. Polypyrrole forms highly oriented tubular whiskers on Nuclepore with striations along the direction of growth having conductivities between 2000 and 3000 S cm^{-1}, higher than those observed in typical preparations of polypyrrole films. On the other hand, poly(3-methylthiophene) forms whiskers with an interesting spiral morphology, having relatively poor conductivities.

Introduction

The degree of preferential orientation that can be achieved in a film prepared from a highly anisotropic polymeric conductor controls the magnitude of its conductivity. It is for this reason that considerable attention has been devoted to the mode of polymerization and to processing conditions in the synthesis of these polymers. In the cases of polypyrrole and polythiophene, variation in conductivity has been achieved by controlling the electrosynthetic conditions, since the polymer itself, once prepared, is intractable. Some substituted polythiophenes are soluble, allowing solution processing techniques to be employed.

One way of controlling the morphology of electrochemically grown materials is to utilize structured, porous substrates. Indeed, Penner and Martin[1] utilized the dielectric membrane Nuclepore as a template for the growth of polypyrrole fibrils. Nuclepore is a polycarbonate or polyester that has been "drilled" by a nuclear process to provide cylindrical pores of 0.015–14.0 μm size. Penner and Martin attempted to fill these pores with conducting polymer to provide conducting pathways through the Nuclepore membrane. They noted some "blooming" of polymer from the surface of the film as well. Bi et al.[2] noted the formation of PPY nucleated at the surface of a wire net anode in a regular array with "hollow bowl" morphology. It occurred to us to attempt the growth of oriented fibrils at the surfaces of these substrates and to correlate measurements of the conductivities with the morphologies of these fibrils.

In related work published while this paper was under review, Cai and Martin[3] stated that PPY and poly(3-methylthiophene) (P3MT) can be synthesized within the pores of Nuclepore via diffusion of monomer and chemical oxidizing agent from opposite sides of the membrane. Thin films are formed on the walls of the pores, which ultimately become larger to appear to fill the pore (although the homogeneity throughout the pore was not as yet studied). Provided that the films on the walls are very thin (less than 200 nm), they report the conductivities, measured by a two-probe technique, of both polymers to be enhanced to values of approximately 10^3 S cm^{-1} (highest value 1550 S cm^{-1}) and surmise the effect to be caused by alignment of the polymers along the pores.

The usual preparation of PPy films from an acetonitrile solution with tetraalkylammonium salts has been studied in great detail,[4] giving conductivities of the order of 100 S cm^{-1}.[5] A conductivity of 400 S cm^{-1} has been reported for films made in a propylene carbonate solution.[6] Satoh et al.[7,8] have made films with a room-temperature conductivity of 500 S cm^{-1} from an aqueous solution with sodium *p*-toluenesulfonate as the electrolyte. Warren et al.[9] have studied the effects of various aqueous dopants,

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and their results suggest that using *p*-toluenesulfonate gives the highest conductivity in as-grown PPy films. Attempts have been made to determine the optimum potential, temperature, pyrrole concentration, and electrolyte concentration for the reaction.[7,8,10,11]

The electrochemical polymerization of polythiophene in acetonitrile or benzonitrile yields material with conductivities of 10–100 and ~100 S cm^{-1}, respectively.[12,13] A comparison of polythiophene, PT, poly(3-methylthiophene), P3MT, and poly(3-ethylthiophene), P3ET, was performed with varying solvent, monomer concentration, electrolyte concentration, electrode materials, and current density, and P3MT shows the highest conductivity, 510 S cm^{-1}.[14]

Experimental Section

Nuclepore, stainless steel mesh, and Celgard 2400 were used to cover the working electrode, which was encased in poly(tetrafluoroethylene), PTFE, in such a way that only the covered portion of the electrode was exposed to the solution. The cell is essentially the same as that used by Roberts and Schultz.[15] PPy was grown in an aqueous solvent on polycarbonate-based Nuclepore, whereas P3MT had to be grown on the polyester-based material, since propylene carbonate, the solvent for its electrolysis, attacks polycarbonate. The mesh size of the stainless steel screen was 200. Celgard 2400 is a polypropylene film with tortuous pores. The pores are rectangularly shaped but not of uniform size. No successful growth was achieved on Celgard for either PPy or P3MT; growth on stainless steel meshes led to fibrillar production, but the quality of the fibrils achieved was much more satisfactory in the Nuclepore experiments.

Anodic electropolymerization of PPy was performed in a one-compartment cell with a stainless steel or a vitreous carbon working electrode and a stainless steel counter electrode. No reference electrode was used. The stainless steel electrodes were highly polished; vitreous carbon electrodes were cleaned between uses with chromic acid. The electrodes were well rinsed with water and placed in an ultrasonic bath for approximately 2 h. Nuclepore with pore sizes between 1.0 and 10.0 μm was employed. The Nuclepore–PPy and stainless steel mesh–PPy composite were made in an aqueous solution with doubly distilled water utilizing 0.05 M pyrrole (Aldrich) and 0.3 M sodium *p*-toluenesulfonate (Fluka). A constant potential of 2.3 V was applied for 1–3 h. The composites were removed from the solution and placed in an ultrasonic bath containing solvent in order to remove the excess electrolyte. The composites were then allowed to dry in air.

Poly(3-methylthiophene) was polymerized in a one-compartment cell with 0.2 M thiophene (Aldrich) in propylene carbonate (Aldrich) with 0.03 M tetraethylammonium hexafluorophosphate (Fluka). The working electrode was a vitreous carbon disk in a PTFE case, and a platinum foil counter electrode was employed. A constant potential of 10 V was applied for 2 days in a nitrogen atmosphere, giving a current density of approximately 10 mA/cm^2. The product was washed with acetone to remove remaining solvent and electrolyte and then stored under vacuum.

The morphology and the dimensions of the fibrils were investigated on a Phillips 501 B scanning electron microscope (SEM). The fibrils were carefully separated and attached with silver paste to a thin insulating substrate with four gold wires stretched across it. The edge of a fibril could be easily visualized, and the thickness measured. Separation was performed by placing the Nuclepore film on which the fibrils grew in an ultrasonic cleaning bath in a small beaker of water. Many of the fibrils detached during ultrasonic agitation; in some cases where they did not free themselves, they were simply cut from the surface of the Nuclepore with a razor blade. The thickness measurements were performed by taking a SEM enlarged photograph and doing six measurements along the edge of a 2–4-μm fibril with a digital calipers, with the error being ±0.3 μm. The temperature dependence of the conductivity between room temperature and liquid nitrogen temperature was determined by using a computerized four-probe conductivity apparatus.

Elemental analysis of PPy (Galbraith Laboratories) showed the composition to be 56.21% C, 4.49% H, 11.38% N, 8.31% S, and 17.79% O. The mole ratio of N:S, showing the level of doping, is 3.13:1, similar to the value of 3.21 reported by Shen et al.[16]

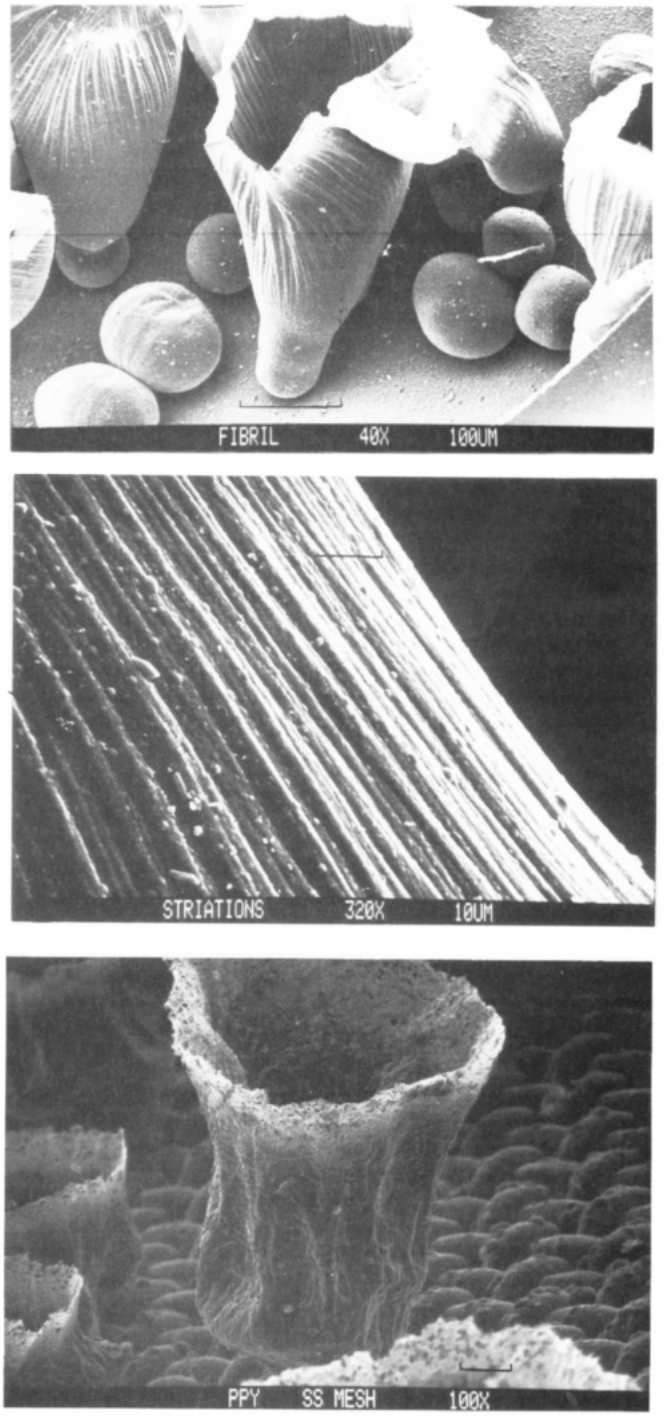

Figure 1. Scanning electron micrographs of PPY fibrils. Upper photo: 40 times magnification, prepared from an aqueous solution on a Nuclepore substrate. Marker = 500 μm. Middle photo: 320 times magnification under the same growth conditions. Marker = 50 μm. Bottom photo: 100 times magnification, prepared from an aqueous solution on a stainless steel mesh. Marker = 100 μm.

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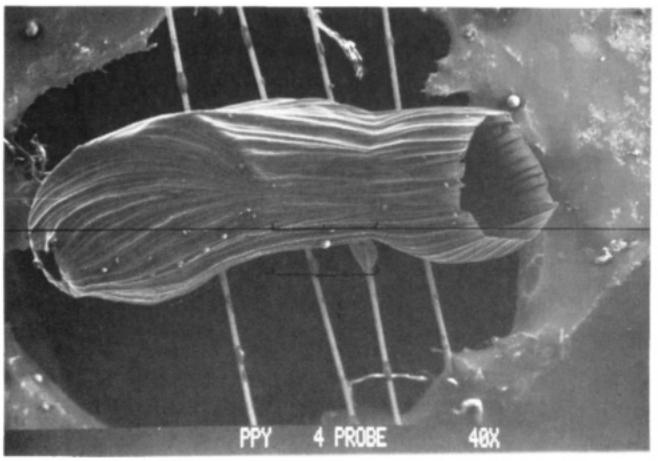


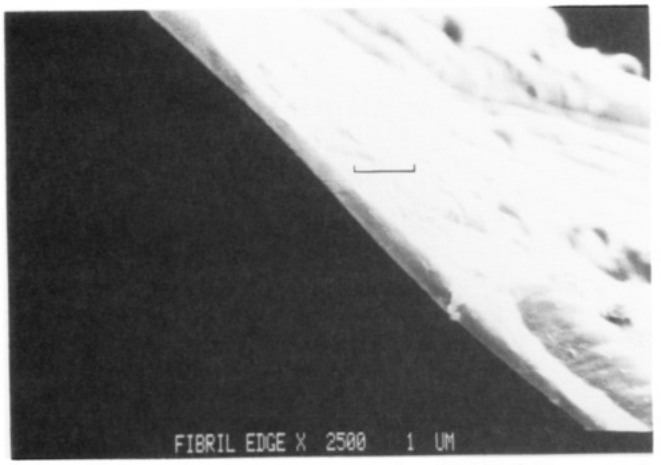


Figure 2. Scanning electron micrographs of PPY fibril mounted with four probes for conductivity measurements (marker = 500 μm) and the edge of a fibril as viewed at high magnification (marker = 5 μm). The conductivity of this particular fibril was 3000 S cm^{-1}. Note that the second and third probes connected to the fibril have pieces of lint that appear to be attached to the probes but were not present during the conductivity measurements.

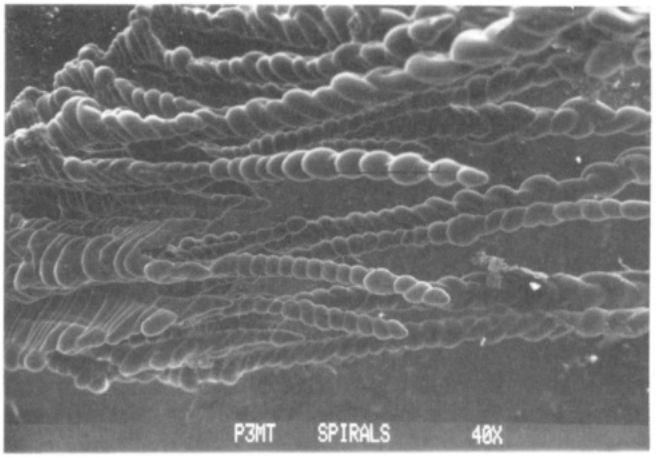
Analyses of the P3MT films were not satisfactory, but further efforts at purification were not made in light of the morphology achieved and the low conductivity.

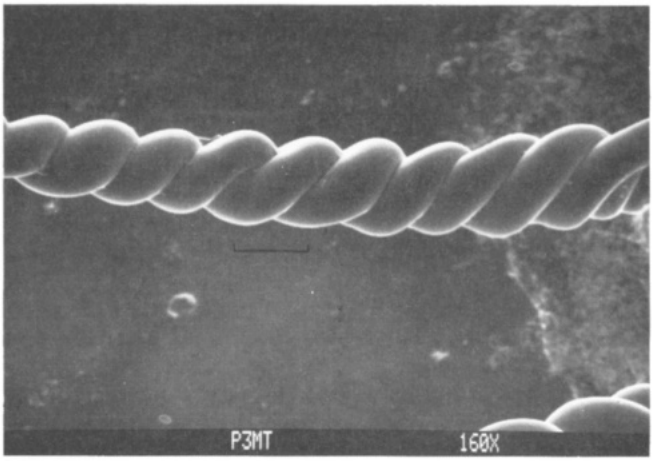
Results and Discussion

Figures 1–3 are SEM photographs of PPY and P3MT fibrils. The PPY tubes grown on Nuclepore (Figure 1) are hollow and show blooming as they grow from the surface (upper photo), and a magnification of the striations (middle photo) on the sides of the bloom show they are extremely regular and well oriented. For comparison, the bottom photo shows the less regular structure of the PPY fibrils grown on a stainless steel mesh. Figure 2 presents views of a mounted fibril with four probes attached, as well as a high magnification view of a fibril edge, which was utilized to obtain the thickness of the fibril. As can be clearly seen, the edge is quite regular and thickness can be determined with accuracy.

P3MT, on the other hand, forms either irregular rodlike fibrils or an interesting twisted, spirallike morphology, shown in Figure 3, when grown on the polyester-based Nuclepore. Both right- and left-handed twists are seen, and the periodicity of the spiral is quite regular.

For both polymers, nucleation probably starts in the pores for the Nuclepore and in the grids for the wire mesh.





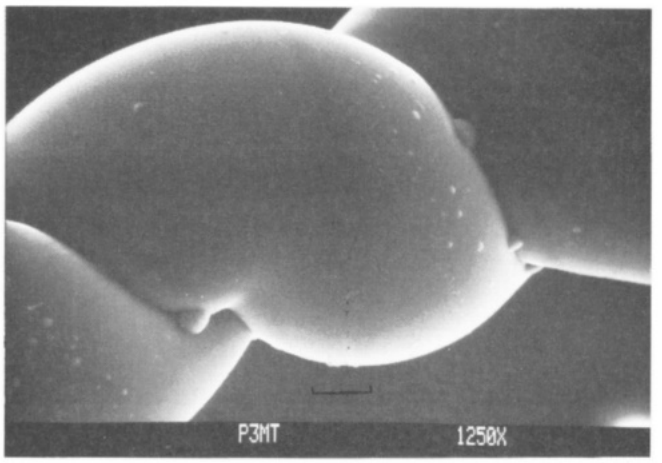


Figure 3. Scanning electron micrographs of P3MT spirals grown on Nuclepore. Top photo: A view of a large number of spirals emerging from the Nuclepore surface. Marker = 500 μm. Middle photo: 160 times magnification, with a left-handed twist. Marker = 100 μm. Bottom photo: 1250 times magnification, with a right-handed twist. Marker = 10 μm.

For the case of PPy, initially a hemisphere is formed. Some of the hemispheres close on themselves, forming a hollow sphere. The other hemispheres begin to propagate as tubes. Vork et al.[17] observed the formation of tubes in the growth of PPY under similar conditions with a bare electrode but not with the same degree of orientation. The dimensions of typical tubes of PPY are approximately 3 mm long and 0.5 mm wide, with the thickness depending on the reaction time. The highly oriented tubes all have a thickness of 2–3 μm. After the P3MT starts propagating

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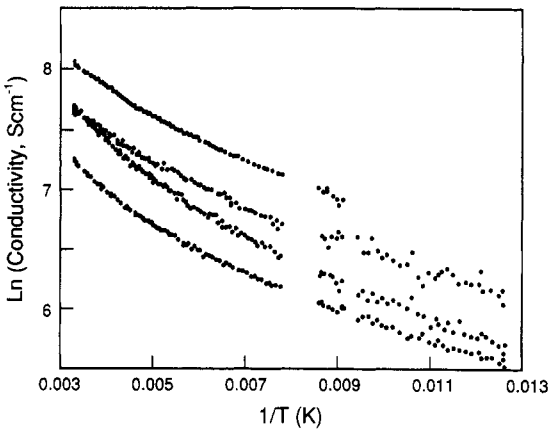

Figure 4. Plot of the natural logarithm of the conductivity of four PPY fibrils as a function of reciprocal temperature (kelvin).

in the pores, propagation continues vertically. The P3MT spirals are up to 5 mm long and approximately 70 μm in diameter.

The samples of PPy are sufficiently large so that four-probe conductivity measurements can be performed along the length of the tubes. Figure 4 is a plot of the temperature dependence of the four-probe conductivity of several samples from room temperature to liquid nitrogen temperature. The room-temperature conductivity of the PPy tubes is the highest reported for this material to date. One sample has a room-temperature conductivity of over 3000 S cm^{-1}. Two other samples have a room-temperature conductivity of over 2000 S cm^{-1}, and a fourth sample had a conductivity of 1300 S cm^{-1}. The conductivity is greatest along the long axis in the direction of the striations. The highest previously reported conductivity for PPy (prepared in propylene carbonate with hexafluorophosphate as the dopant) is 1550 S cm^{-1} reported by Yamaura et al.[6] for films oriented by stretching 2.5 times.

It is apparent that the orientation necessary to achieve high conductivity in PPY grown on Nuclepore is not restricted to the walls within the cylindrical pores and is not restricted to extremely thin films, as claimed by Cai and Martin.[3] Rather it appears that the nucleation conditions tend to promote oriented growth even outside the pores. It must be commented that since the measurements performed by Cai and Martin[3] could not be accomplished by four-probe methodologies, deducing such high conductivities of such extremely thin samples from two-probe measurements must be regarded as highly speculative.

Estimates of the conductivity perpendicular to the striations were extremely difficult due to the dimensions of the sample but appear to be at least an order of magnitude lower. Ogasawara et al.[18] report an anisotropy of about 5 for stretched PPy films.

The activation energy calculated for the four samples ranges from 14.4 to 18.7 meV. Although curvature of the Arrhenius plots is evident, averaging all values in the temperature range from room temperature to liquid nitrogen gives values of 0.0173 ± 0.002 eV, 0.0144 ± 0.002 eV, 0.0157 ± 0.002 eV, and 0.0187 ± 0.002 for the four samples. These numbers are slightly higher than the value of 4.1 meV reported by Satoh et al.[7,8]

Because of the low conductivity of the P3MT samples, only two-probe measurements at room temperature were taken. The values of conductivity along the long direction are consistently close to 3×10^{-4} S cm^{-1}.

Conclusions

Pyrrole polymerized on electrodes covered with Nuclepore in an aqueous solution with *p*-toluenesulfonate as the electrolyte forms oriented PPy whiskers, with conductivities that are very high as compared to normal preparations. 3-Methylthiophene polymerized on vitreous carbon electrodes covered with Nuclepore in propylene carbonate with tetraethylammonium hexafluorophosphate as the electrolyte forms spiral rods, which show no preferential twisting direction. The use of special template surfaces to control nucleation and growth in polymeric conductors warrants further investigation.

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Registry No. PPy, 30604-81-0; P3MT, 84928-92-7; Nuclepore, 12673-61-9; stainless steel, 12597-68-1.

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