Template Synthesis of Conducting Polymeric Nanocones of Poly(3-methylthiophene)

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The electrochemical synthesis of conducting poly(3-methylthiophene) nanocones on carbon cloth, employing an alumina membrane as a template, is reported. The morphological characterization has been done using high- resolution transmission electron microscopy and scanning electron microscopy for both the template-synthesized and the template-free poly(3-methylthiophene). The morphology of the template-synthesized poly(3-methylthiophene) varies from hollow oriented nanocones to deformed nanocones and agglomerated forms (not in cone form) depending on the experimental conditions. The electrochemical properties of the nanocone electrode have been compared with those of the conventionally synthesized poly(3-methylthiophene) on carbon cloth, using cyclic voltammetry and impedance spectroscopy. The impedance and cyclic voltammetric measurements revealed that there is a rapid charge transport within the nanocones and between the nanocones and the electrolyte. The low impedance of dendritic poly(3-methylthiophene) nanocones is promising for their application in polymer electrolyte membrane fuel cells, where the internal resistances need to be minimized.

I. Introduction

Since the discovery of the organic conducting polymers more than 20 years ago,[1] these materials are finding more and more applications in various branches of technology, such as metalization of dielectrics,[2] primary and secondary batteries,[3] antistatic coatings,[4] electromagnetic shieldings,[5] electrocatalysis,[6] electrochromic devices,[7] chemical sensors,[8] etc. It is established that thin layers of conducting polymers on the surface of substrate electrodes are able to enhance the kinetics of various electrode processes.[9] The catalytic activity of noble metals, widely used in a variety of applications, is known to depend highly on their dispersion and surface properties. Conducting polymers have therefore been considered to be useful matrices for the immobilization[6] of dispersed noble metal catalysts. Further, with the advancement of nanotechnology, several nanostructured conducting polymers (viz. nanotubues and nanofibrils) have been made in order to exploit their unique properties in nanoscale electronic and molecular devices. One approach for building such nanoscale matrices involves the use of nanoporous host materials as templates.[10] Nanoporous templates like polycarbonates and alumina membranes have been effectively utilized to prepare conducting polymeric nanotubules or fibers of polyaniline,[11] polypyrrole,[12] poly(3-methylthiophene),[13] and polyacetylene on gold or platinum substrates.[14,15] It has been reported[13] that these polymers have enhanced conducting and charge transport properties compared to the conventionally synthesized conducting polymers. The nanotubules and nanofibers of conducting polymers can also be assembled in a variety of architectures for different applications.[10]

We report here, for the first time, the synthesis and characterization of conducting polymeric nanocones of poly(3-methyl)thiophene using nanoporous alumina membranes as templates on commercially available carbon cloth. The carbon cloth can serve as the gas diffusion electrode or as a backing layer in one of the major emerging nonconventional energy applications, namely the polymer electrolyte and direct methanol fuel cells.[16] We also evaluated and compared the morphological and electrochemical properties of the poly(3-methylthiophene) synthesized on carbon cloth without the templates.

II. Experimental Methods

A. Substrate Preparation. A 2.5 cm^2 rectangular strip of commercially available uncatalyzed carbon-coated carbon cloth (E-TEK) was coated with 30 μL of 5 wt % Nafion as a thin layer. The Nafion-coated area was 0.3 cm^2, and the remaining area was insulated except for the electrical connection. The alumina membrane (pore diameter = 0.2 μm; membrane thickness = 60 μm and porosity = 65%), Anapore pore filter (Whatman, U.S.A.) was placed on the Nafion-coated carbon cloth and hot pressed at 393 K for 2 min at a pressure of 50 kg/cm^2. This configuration of alumina (Al$_2$O$_3$) membrane attached Nafion-coated carbon cloth (CC) was designated as CC/Naf/Al$_2$O$_3$. The contact area of the working electrode in the case of template-attached carbon cloth, taking into account the percentage of porosity, was found to be 0.195 cm^2.

B. Electropolymerization of 3-Methylthiophene on CC/ Naf/Al$_2$O$_3$. The electropolymerization was carried out in acetonitrile, using 0.1 M 3-methylthiophene and 0.2 M tetrabutylammonium tetrafluoborate, in a potentiodynamic mode by sweeping the potential between 0.1 and 1.5 V vs Ag/AgCl at 200 mV/s. The charge passed between 1.2 and 1.5 V was recorded and denoted as the polymerization charge.[17] The

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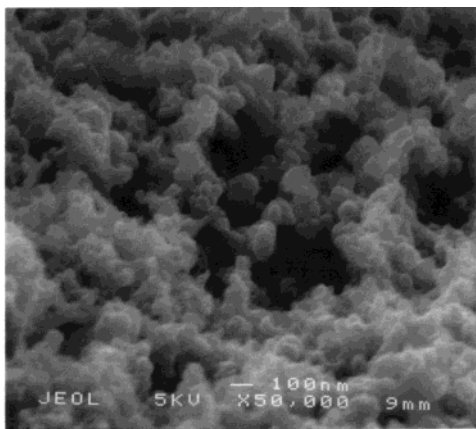⊥ Indian Institute of Technology.

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Figure 1. Scanning electron micrograph of Nafion coated on a commercial carbon cloth.

thickness vs density relationship[18] has been used to calculate the relative mass of the polymer deposited.

C. Removal of Template. The alumina membrane in CC/Naf/Al$_2$O$_3$/PMT$_{Temp}$ was removed by immersing the composite in 0.1 M NaOH for 15 min. The composite after the dissolution of the template was repeatedly washed with deionized water to remove the residual NaOH. It was subsequently immersed in 1% HBF$_4$ for 10 min and then washed with deionsed water again. The composite after the dissolution of the template (CC/Naf/PMT$_{Temp}$) was kept at -0.8 V for 360 s. Holding the potential at -0.8 V reduces the oxidized poly(3-methylthiophene). Immersion in HBF$_4$ followed by the reduction at -0.8 V probably causes the expulsion of OH$^-$ ions introduced during the dissolution of the template by NaOH. These steps help to restore the polymer to its original redox behavior. The OH$^-$ ions have shown to have a deleterious effect on the redox behavior of poly(3-methylthiophene), as was observed with polypyrrole.[12] The conventionally synthesized template-free poly(3-methylthiophene) was designated as CC/Naf/PMT. In both template-based and template-free cases, the Nafion applied on the electrode surface is present even after removing the template.

D. Electrochemical and Spectroscopic Measurements. The electrochemical measurements were performed using a Wenking Potentioscan (POS 73) with a Philips X-Y recorder (PM 8033). Pt foil (1 cm^2) and Ag/AgCl were used as counter and reference electrodes, respectively. The working electrode was varied according to the requirement. The impedance measurements were made using a Solartron SI 1225 HF frequency response analyzer along with an EG&G M398 software program, between 100 kHz and 0.01 Hz, with an ac modulation of 5 mV peak-to-peak overlaid on a dc bias potential and the impedance data were obtained at a rate of 10 points per decade of frequency. The ohmic resistances were calculated from the intercept on the X axis (Ω) normalized to the unit area (cm^2).

III. Results and Discussion

A scanning electron micrograph (SEM) of the Nafion-coated carbon cloth is shown in Figure 1. The dense and globular coverage of Nafion on the carbon cloth is revealed in the SEM image. The advantages of coating Nafion on the carbon cloth are 2-fold: it not only acts as a binder for the alumina membrane attachment to the carbon cloth, but also provides the protonic transport to the electronic conductive carbon matrix. This configuration proves to be very important for enhancing the performance of electrodes in fuel cell applications.

Parts a−c of Figure 2 show the HR-TEM images of template-synthesized poly(3-methylthiophene) with a polymerization charge of 300 mC/cm^2, over 375 s. It is quite interesting to see completely the unusual nanocone morphology of the poly(3-methylthiophene).[16] Figure 2a distinctly shows a well arranged hollow cone-in-cone and cone-over-cone structure. Figure 2b shows clearly the open end of one cone and the apex inserted into the next cone, with the outer diameter of the nanocone almost matching with the pore diameter of the template used (200 nm). These bunches of nanocones are distributed throughout the carbon grid as revealed from Figure 2c. The average nanocone length was found to be 1.6 μm, though the growth of a single nanocone can take place over the entire width of the membrane. The scanning electron micrograph, shown in Figure 2d, of poly(3-methylthiophene) synthesized by template-free method reveals rather a dense agglomerated globular morphology.

The nanocone morphology did not change significantly when the polymerization charge was changed from 300 (300 s) to 600 mC/cm^2 (750 s), but a deformation in the nanocone was observed when the polymerization charge was further increased to 700 mC/cm^2 (875 s). When the polymerization charge was further increased to 1000 mC/cm^2, a dense deposit of poly(3-methylthiophene) resulted, with only few nanocones projecting from the carbon cloth substrate. This revealed that there is an optimum range of charge, beyond which the nanocone morphology is not retained. However, the variation of the monomer concentration between 10^{-2} and 0.1 M did not alter the nanocone morphology much.

Even though the template synthesis is normally expected to direct the growth of the polymer in tubular form, in the past other geometries have also been observed: such as pancake, nanoplug, and others.[19,20] The exact mechanism of the nanocone formation is not yet known.

Figure 3 shows the cyclic voltammogram of the polymerization of 3-methylthiophene on a template-attached carbon cloth. The oxidation potential of 3-methylthiophene begins at $+0.7$ V with the formation of polymer at the electrode surface. The cyclic voltammogram also exhibits broad anodic and cathodic peaks corresponding to the oxidation and the reduction of the preformed polymer. The peak current densities increase proportionally with the number of scans. This is characteristic of the formation of a conductive and electroactive polymer on an electrode surface. The cyclic voltammogram observed with the polymerization of 3-methylthiophene (template free) is similar to that reported in the literature.[17]

A difference in peak splitting was observed for both the electrodes during the polymerization. This might be due to an IR drop occurring across the electrode/electrolyte interface. This IR drop could also arise from the Teflonized carbon cloth, which served as the substrate. Further, the Nafion, which was used to bind the alumina membrane on the carbon cloth, also can cause an IR drop. A more detailed investigation is required to understand the effect of Nafion on the polymer deposition and the electrochemical characteristics of poly(3-methylthiophene).

The cyclic voltammogram (CV) of CC/Naf/PMT$_{Temp}$ (see Methods) after the immersion in 1% HBF$_4$ is shown in Figure 4a. The characteristic peak due to oxidation of poly(3-methylthiophene) is observed at $+0.51$ V and the corresponding reduction is at $+0.48$ V. The CV of the template-free poly(3-methylthiophene) electrode (CC/Naf/PMT) is shown in Figure 4b. The nature of the voltammogram is similar to that of the poly(3-methylthiophene) synthesized by the template method. However, the oxidation appeared at $+0.59$ V and the corre-
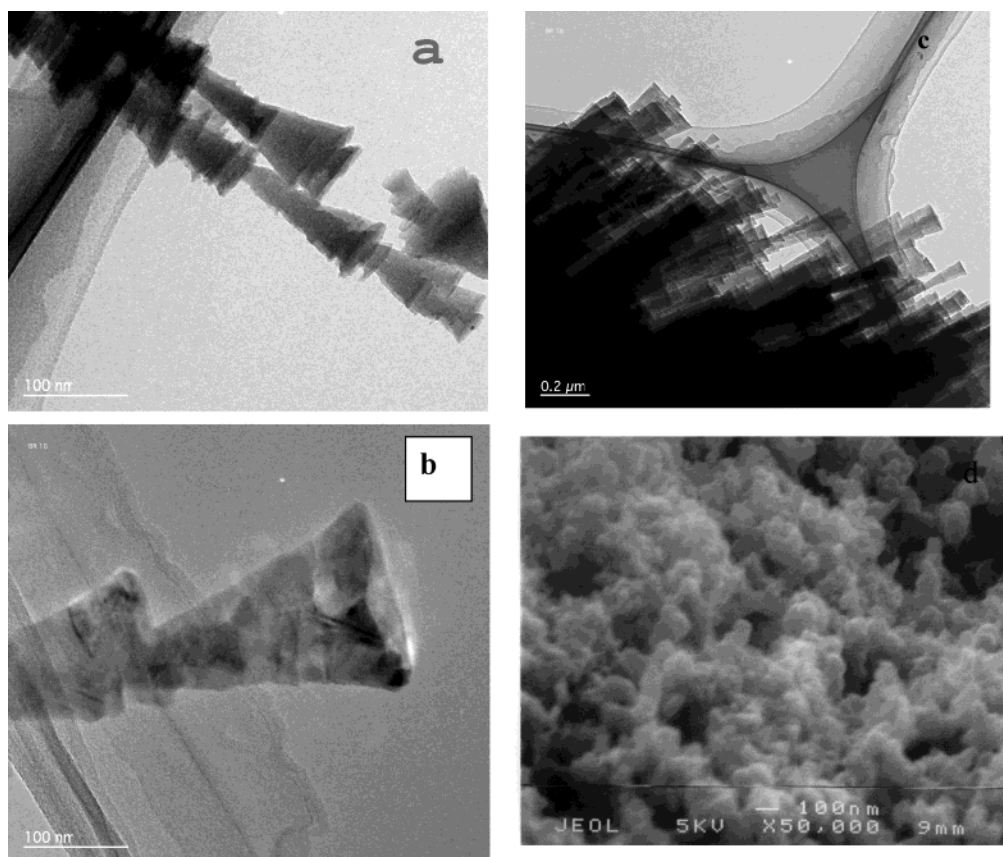
Figure 2. Electron micrographs of template-based and template-free poly(3-methylthiophene): (a−c) HR-TEM images of template-based poly(3-methylthiophene) nanocones; (d) SEM of template-free poly(3-methylthiophene). The charge used for the polymerization was 300 mC/cm^2.
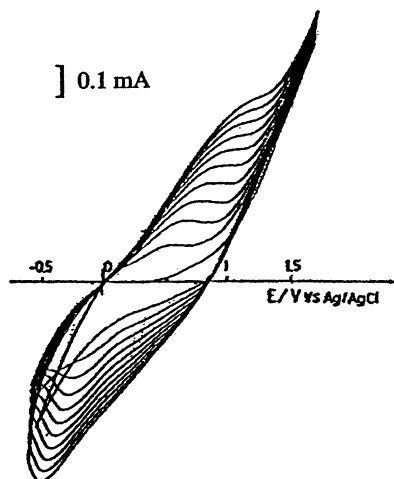

Figure 3. Cyclic voltammogram of polymerization of 0.1 M 3-methylthiophene in acetonitrile when using 0.2 M tetrabutylammonium tetrafluoborate as electrolyte and alumina membrane as the template. Scan rate 200 mV/s.

Figure 4. CVs of poly(3-methylthiophene) electrodes in 1 M H$_2$SO$_4$. Scan rate 50 mV s^{-1}. (a) Template-based poly(3-methylthiophene) (24 μg) nanocones. (b) Template-free poly(3-methylthiophene) (36 μg).

sponding reduction at +0.29 V. The current response obtained for the nanocone electrode was higher compared to the non-nanocone electrode. The higher current response of the nanocone electrode is consistent with a much higher contact area between the dendritic poly(3-methylthiophene) and the electrolyte than that is available in the untemplated poly(3-methylthiophene) coating. The difference between the peak potentials of the template-free poly(3-methylthiophene) was higher (300 mV) than the difference (30 mV) between the peak potentials on the template-synthesized nanocone electrodes. To examine whether the process is diffusion-controlled or kinetic-controlled, the cyclic voltammograms were run at different scan rates for both
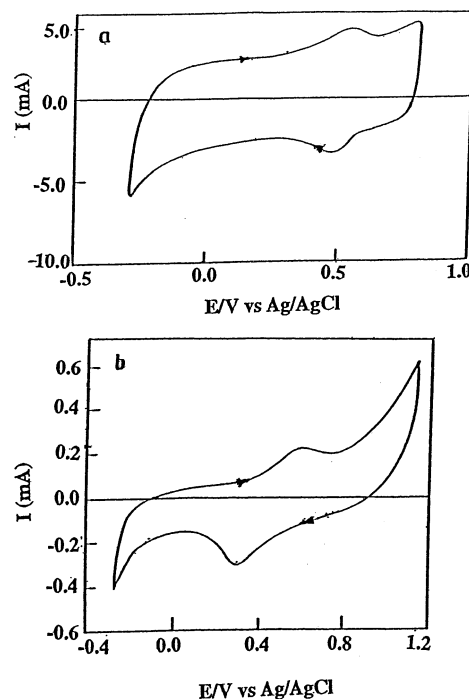
the electrodes (template based and template free) and the anodic peak currents plotted against scan rates. The peak current varies linearly with the scan rate registering a slope of 0.8 mA/(V/s) for the template-synthesized nanocone electrode, but for the template-free poly(3-methylthiophene) electrode, it varies lin-
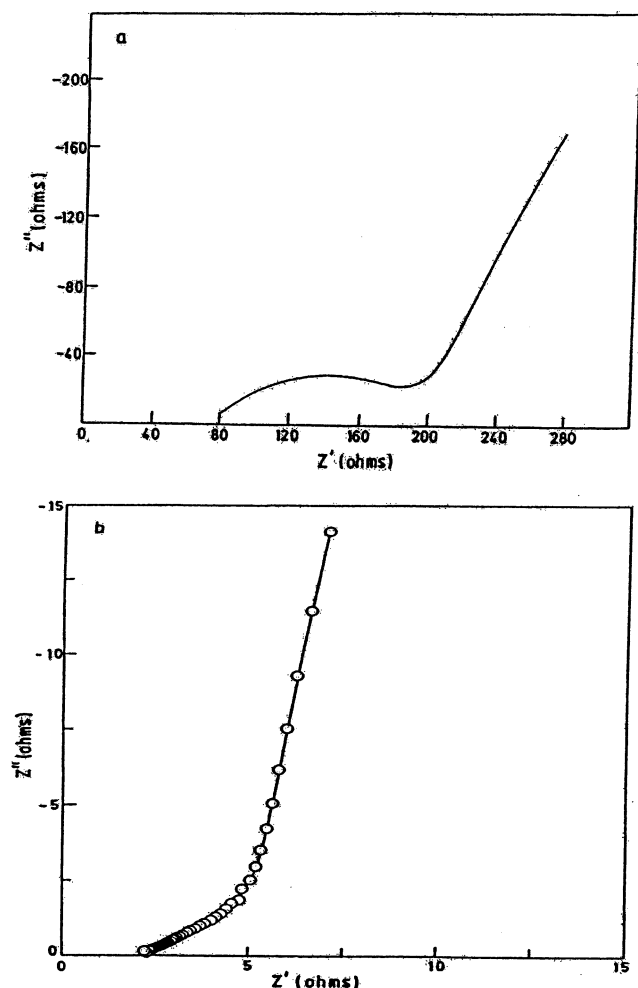
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Figure 5. Nyquist complex-plane impedance plot obtained for (a) CC/Naf/PMT (templatefree) and (b) CC/Naf/PMT$_{Temp}$ electrodes, at +0.6 V in 1 M H$_2$SO$_4$.

early with the square root of scan rate with a slope 0.65 mA/(V/s)$^{1/2}$. The data indicate that the current is diffusion-controlled due to limitations in charge transport within the untemplated poly(3-methylthiophene). Another observation made from the scan rate dependence study of cyclic voltammetry was that the peak potential was nearly independent of the scan rate for the templated polymer, whereas the peak splitting was systematically increased with scan rate for the untemplated polymer. These are some of the manifestations of the different rates of charge and ion flow in the two morphologies of the polymer. The two observations (linear peak current with scan rate and peak potential independent of the scan rate) for the dendritic poly(3-methylthiophene) indicate that charge transport within each dendrite and across the polythiophene−electrolyte interface is rapid on the time scale of the experiment. Given the aspect ratio of the dendrites (length considerably greater than the diameter), these results suggest that charge transport within the poly(3-methylthiophene) is remarkably fast. The cyclic voltammogram[21] of the Nafion-coated carbon layer did not exhibit any peak between −0.8 and +0.8 V vs Ag/AgCl, which confirmed that the peaks observed in the cyclic voltammograms (Figure 4, parts a and b) are due to poly(3-methylthiophene).

The impedance spectra recorded at +0.6 V shown in Figure 5a of CC/Naf/PMT reveals a semicircle at high frequencies with an ohmic resistance of 23.4 Ω cm^2 (intercept on *X* axis (Z′) normalized per unit area). (Since the use of dendritic poly(3-methyl)thiophene is anticipated in direct methanol fuel cells,

+0.6 V vs Ag/AgCl has been chosen based on the peak potential of methanol oxidation observed in the cyclic voltammogram.) The impedance spectra of CC/Naf/PMT$_{Temp}$ recorded at +0.6 V is shown in Figure 5b. The 0.41 Ω cm^2 (intercept on *X*-axis (Z′) axis normalized per unit area) for the templated polymer coating is the sum of the resistances in the carbon cloth, possibly across the Nafion membrane, and possibly along the dendrtic polymers. The 23.4 Ω cm^2 for the untemplated poly(3-methylthiophene) is attributable to charge transport in that polymer coating. Both resistances are in good agreement with the observed behavior in the cyclic voltammogram. Though both systems tend toward a capacitive behavior, the capacitive nature is more pronounced for templated polymer because the angle of the line at low frequencies is close to 90° compared to untemplated polymer. The impedance behavior of the templated polymer is consistent with a dendritic structure with high charge conductivity along the dendrites. However, a more detailed analysis requires an elaborate model and a full mathematical treatment, which is currently in progress. Whatever model is used to interpret the impedance behavior of the dendritic poly(3-methylthiophene), it is clear from Figure 5b that kinetic processes are very fast because all the associated impedances are quite low. The low impedance suggests the application of the nanocone poly(3-methylthiophene) in polymer electrolyte membrane fuel cells, where all the internal resistances should be minimized.

IV. Conclusions

The electrochemical synthesis and characterization of conducting poly(3-methylthiophene) nanocones on carbon cloth, using alumina membrane template, is reported here. The observed superior electrochemical properties are due to remarkably fast charge transport in dendritic poly(3-methylthiophene) in comparison to the template-free poly(3-methylthiophene). This is attributed to the nanocone morphology of the template-synthesized poly(3-methylthiophene) electrodes. Since the conducting polymer can be employed as a dispersive matrix for noble metal particles, we are currently investigating platinum nanoparticles incorporated in poly(3-methylthiophene) as an electrode material for methanol oxidation in fuel cells.

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