2474 *Chem. Mater.* **2010,** *22,* 2474–2480
DOI:10.1021/cm902986g

CHEMISTRY OF MATERIALS
Article

Deposition of Ultrathin Coatings of Polypyrrole and Poly(3,4-ethylenedioxythiophene) onto Electrospun Nanofibers Using a Vapor-Phase Polymerization Method

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Received September 25, 2009. Revised Manuscript Received January 29, 2010

Electrospun polyacrylonitrile (PAN) nanofibers were successfully coated with polypyrrole (PPy) or poly(3,4-ethylenedioxythiophene) PEDOT layers. To obtain ultrathin coatings on highly porous nanofibrous webs, we adapted a two-step vapor-phase coating process usually used to produce ultrathin films. Ferric tosylate (FeTos) was chosen as the oxidant, because of its solvent-free templating effect that produces highly ordered polymer coatings with improved electronic properties. The concentration of the oxidant solution was found to be a key parameter for the preservation of the open porosity in the nanofibrous mats. Coating thicknesses varied from 5 to 12 nm depending on the polymer and oxidant concentrations. The coatings were strongly attached to the PAN nanofibers and presented some degree of crystallinity and high conductivities. PEDOT-coated nanofibers displayed good electrochemical properties without the need of an additional current collector, making them excellent candidates for the fabrication of flexible electronic devices.

Introduction

Electrospinning is the most common method for the production of polymer nanofibers and nanofibrous nonwoven mats, because of its simplicity, versatility, and relatively low cost. Electrospun materials find applications in numerous areas, such as ultra- and active filtration, biological cell growth, drug delivery, wound healing, catalysis systems, battery-separators, etc. Several recently published reviews detail the technology and applications of electrospun nanofibers.[1−3] More specifically, significant efforts are being deployed to develop conductive nanofibrous materials for applications in areas such as electrochromic devices,[4] active coatings,[5] sensors,[6] actuators,[7] and energy storage.[8]

However, the electrospinning of conductive nanofibers is not trivial and different strategies have been studied to produce them. The composite approach consists in the incorporation of conductive particles such as carbon nanotubes (CNT) into the fibers.[9−12] However, the dispersion of the CNTs represents a major challenge that can be solved only by specific CNT surface chemistries, in order to increase their affinity for the polymer matrix. A second method consists in electrospinning intrinsically conducting polymers (ICPs), such as polythiophenes,[13,14] polypyrrole,[15,16] polyaniline,[17−19] or poly(*p*-phenylenevinylenes).[20,21] However, these polymers are usually too stiff to be electrospun by themselves. Therefore, blending the ICPs with another electrospinnable polymer is generally required to obtain nanofibers, but to the detriment of the electronic properties. A third method consists of coating electrospun nanofibers with conductive materials. For example, Han and co-workers deposited gold layers onto PAN and PMMA electrospun nanofibers by an electroless plating method and

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Published on Web 03/31/2010

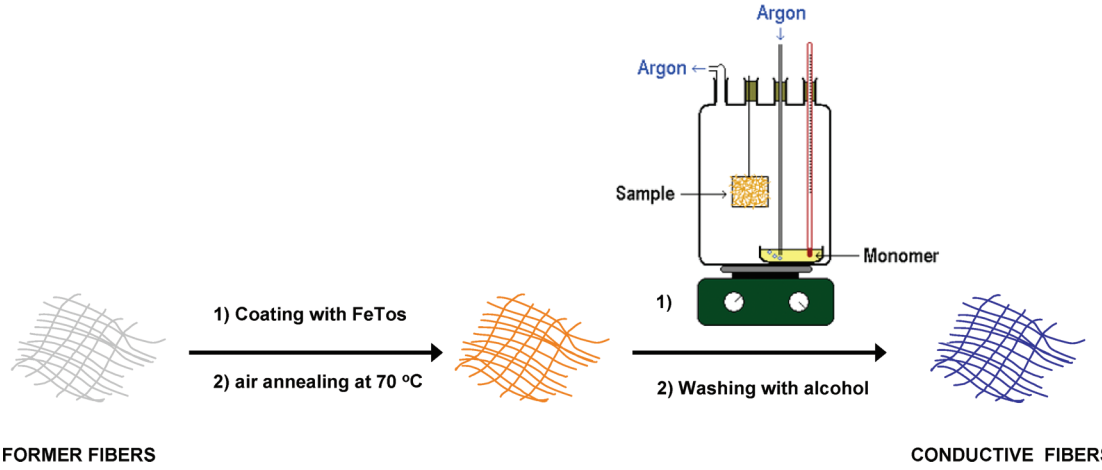

Figure 1. Two-step, vapor-phase ICP coating process.

reported conductivities greater than 1×10^4 S/cm.[22,23] Havel et al. coated polyamide electrospun nanofibers with multiwalled CNTs by a simple dipping procedure.[24] Several groups reported the deposition of ICP layers onto electrospun materials by in situ polymerization techniques, where the electrospun fibers were successively coated by oxidant and monomer layers, in solution or vapor form.[5,7,25−30] This method is very flexible and essentially allows the addition of electronic properties to any electrospun material (with optimized mechanical properties) using standard coating deposition procedures.

In this work, we studied the deposition of ultrathin layers of polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) onto PAN electrospun nanofibers. We used a simple two-step, vapor-phase method to produce ordered and ultrathin ICP coatings. This method allowed the fabrication of the thinnest ICP coatings on nanofibers reported to date, demonstrating very high conductivities.

Experimental Section

Materials. Polyacrylonitrile powder (~150 000 g/mol; d = 1.184 g/cm^3) as well as pyrrole, acetonitrile (99%, anhydrous), dimethylformamide (DMF, 99%, Biotech grade), and tetrabuthylammonium hexafluorophosphate (NBu_4PF_6, 99%) were purchased from Sigma-Aldrich. A solution of ferric(III) *p*-toluenesulfonate (FeTos) at 40 wt % in butanol as well as 3,4-ethylenedioxythiophene (EDOT) were obtained from HC Starck (under the respective trade names Clevios CB40 and Clevios M).

Methods. Polyacrylonitrile (PAN) nanofibers were obtained by a conventional electrospinning method: a 12 wt % PAN solution in DMF was placed in a syringe and electrospun at 1 mL/h on a polyimide supporting sheet placed on a rotating metallic collector. The distance between the tip of the syringe needle and the collector was 15 cm and the voltage applied was 40 kV. The electrospinning process was very stable and allowed the continuous production of very uniform PAN nanofibers over several hours. Sheets (30×50 cm^2) of nonwoven mats with thicknesses around 100 μm were obtained after 7 hours of continuous electrospinning on the substrate rotating and translating at low speed, ensuring a homogeneous thickness over the whole deposition area. The nanofiber mats were peeled off the polyimide supporting sheet using a scalpel.

The ICP coating process is described in Figure 1. The electrospun mats were dipped into a FeTos solution. The excess of FeTos solution was gently wiped off with a tissue and the coated mat was annealed in air at 70 °C on a hot plate for 5 min. The mat was then introduced in a reactor where argon was bubbled through the liquid monomer. The monomer vapors polymerized when they came in contact with the FeTos-coated nanofibers, producing a thin ICP coating, doped with tosylate anions. In the PEDOT coating procedure, 0.5 mol of pyridine per mole of FeTos was added to the oxidant solution in order to prevent the occurrence of an acidic side-reaction during the vapor-phase polymerization.[31] The polymerization time and temperature were varied depending on the monomer used: pyrrole polymerized at ambient temperature within a few minutes, as revelead by the appearance of the characteristic black color of polpyrrole. The polymerization time for PPy was then fixed to 15 min. On the other hand, EDOT, which has a higher oxidative potential and a lower vapor pressure than pyrrole, was polymerized at 60 °C during 1.5 h to ensure a complete polymerization.

Characterization. Scanning electron microscopy (SEM) was performed on a Hitachi S4700 microscope, and transmission electron microscopy (TEM) on a Philips CM200 microscope at 200 kV. X-ray diffraction patterns were acquired using a Bruker AXS D8 Discover diffractometer with a Cu Kα radiation source (λ = 1.54 Å). Four-point probes conductivity measurements were performed on a homemade device consisting on four parallel platinum wires positioned 0.2 cm away from each other,

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Table 1. Composition, Fiber Diameter, Porosity, and Conductivity of the PAN Electrospun Mats Coated with PPy or PEDOT

	uncoated	PEDOT-coated			PPy-coated		
FeTos concentration (wt %)		13	20	40	13	20	40
mat composition (wt %)	100 PAN	91 ± 2 PAN 9 ± 2 PEDOT	79 ± 2 PAN 21 ± 2 PEDOT	66 ± 3 PAN 33 ± 3 PEDOT	91 ± 1 PAN 9 ± 1 PPy	84 ± 2 PAN 16 ± 2 PPy	75 ± 3 PAN 25 ± 3 PPy
fiber diameters (nm)	280 ± 29	290 ± 31	294 ± 33		299 ± 35	304 ± 30	
estimated coating thickness (nm)		5	7		10	12	
estimated porosity (%)	85	84	82	79	83	82	79
conductivity (S/cm)		1.0 ± 0.5	8 ± 3	26 ± 6	0.07 ± 0.02	0.10 ± 0.02	1.5 ± 0.1

connected to a VMP3 multipotentiostat (BioLogic, Inc.). A range of current intensities were applied to the two external probes and the corresponding voltage drops between the two internal probes were measured.

The porosity (P) of the uncoated mats was determined using the following equation

$$P = \frac{(d_0 - d)}{d_0} \times 100$$

where d_0 is the PAN density (1.184 g cm^{-3}, as specified by the provider) and d the apparent density, calculated using the mass and geometrical dimensions of each sample. In the case of coated mats, the density, d_0, was calculated according to the percentage of each component (obtained from the mass difference between coated and uncoated mats) and varied for each sample. The density of tosylate-doped PPy and PEDOT have been reported to be 1.35 and 1.64 g cm^{-3}, respectively, and these values were used for the estimation of the coating's density.[32,33] The sample thicknesses were measured with a Mitutoyo micrometer having a precision of 0.1 μm. For maximum accuracy in the thickness variations, the measurements were carried out on the exact spots where the coatings were subsequently deposited. Three porosity measurements were carried out for each sample and the data reported in Table 1 represent the average values.

Electrochemical characterization was performed with a VMP3 multipotentiostat using a three-electrode configuration. The electrospun mat was connected using a simple alligator clip. The counter electrode was a platinum grid and the reference electrode an Ag/AgCl NaCl saturated electrode. The electrolyte was NBu_4PF_6 0.1 M in acetonitrile. Electrochemistry was performed in a closed electrochemical cell in ambient conditions.

Mechanical properties were tested with an Instron Microtester model 5548 with a 5 N cell, at an elongation rate of 10 mm/min, and at a temperature of 23 °C. The samples were cut with a length of 60 mm and a width of 3 mm.

Results and Discussion

Morphological Analysis. PAN nanofiber mats were electrospun as described in the Experimental Section. Small pieces of PAN mats were then coated by ICP layers (see Experimental Section). Figure 2a shows pictures of PAN nanofibers, uncoated (left), as well as coated with PEDOT (middle) or PPy (right). The color of the nanofiber mat was characteristic of the polymer present at the surface: uncoated PAN nanofiber mats had a white color, whereas PEDOT-coated mats were light blue and PPy-coated mats displayed a gray color. The white sections at the top of the PPy and PEDOT-coated mats are areas that were not covered by the oxidant solution and were used to fix the samples in the VPP chamber. The coatings appeared uniform and homogeneous over the whole covered area. The overall thickness of the mats was not affected by the wet-coating process, which is expected because PAN is not swollen in alcohols.

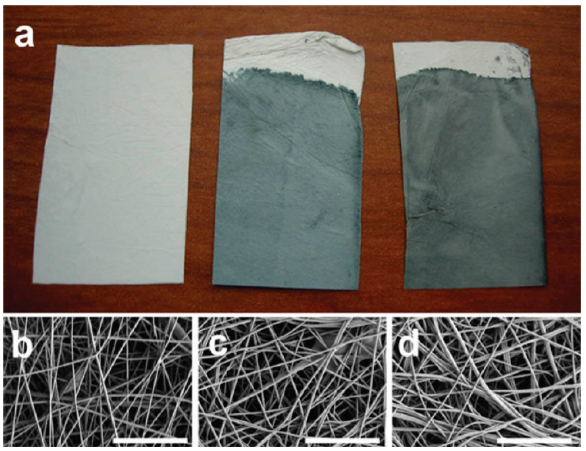

Figure 2. (a) Photograph and (b–d) SEM micrographs of PAN nanofiber mats (b) uncoated and coated with (c) PEDOT or (d) PPy using 13 wt % oxidant solution. The mats are approximately 4 × 2.3 cm^2; SEM scale bars represent 10 μm.

Figure 2b–d presents SEM micrographs of the corresponding fiber mats, showing almost no change in fiber geometry upon coating. However, the oxidant concentration had to be carefully controlled in order to preserve the porosity of the mats. Figure 3 shows the SEM images of the mats coated using different oxidant concentrations.

When the commercial oxidant solution was used (40 wt % FeTos in butanol), the viscosity of the coating was high and the excess of oxidant could not be efficiently wiped off from the mat. Consequently, the ICPs polymerized as thick films covering the surface of the mat (cf. Figure 3a,d). It is interesting to point out that the global porosity of the covered mats, calculated by the weighting technique (see the Experimental Section), was still around 80% (from a porosity of 85% for the uncoated PAN mat, see Table 1). This latter result implies that despite the fact that the surface porosity was hindered, the internal part of the mats was still highly porous. Indeed, the

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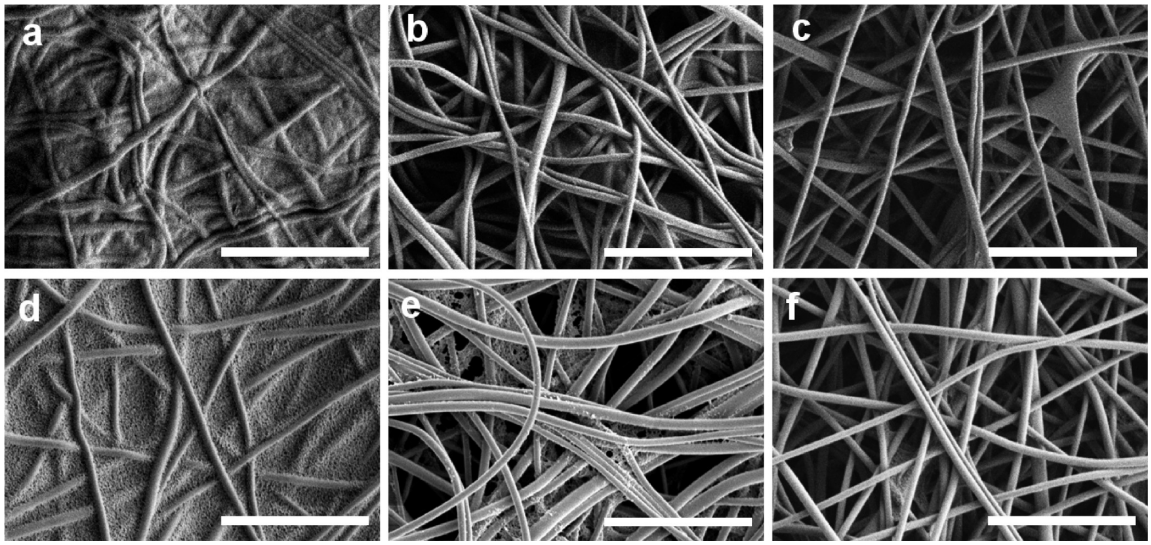

Figure 3. SEM micrographs of PAN nanofibers coated with (a−c) PEDOT or (d−f) PPy using different oxidant solution concentrations: (a,d) 40 wt %, (b,e) 20 wt %, (c, f) 13 wt %. Scale bars represent 5 μm.

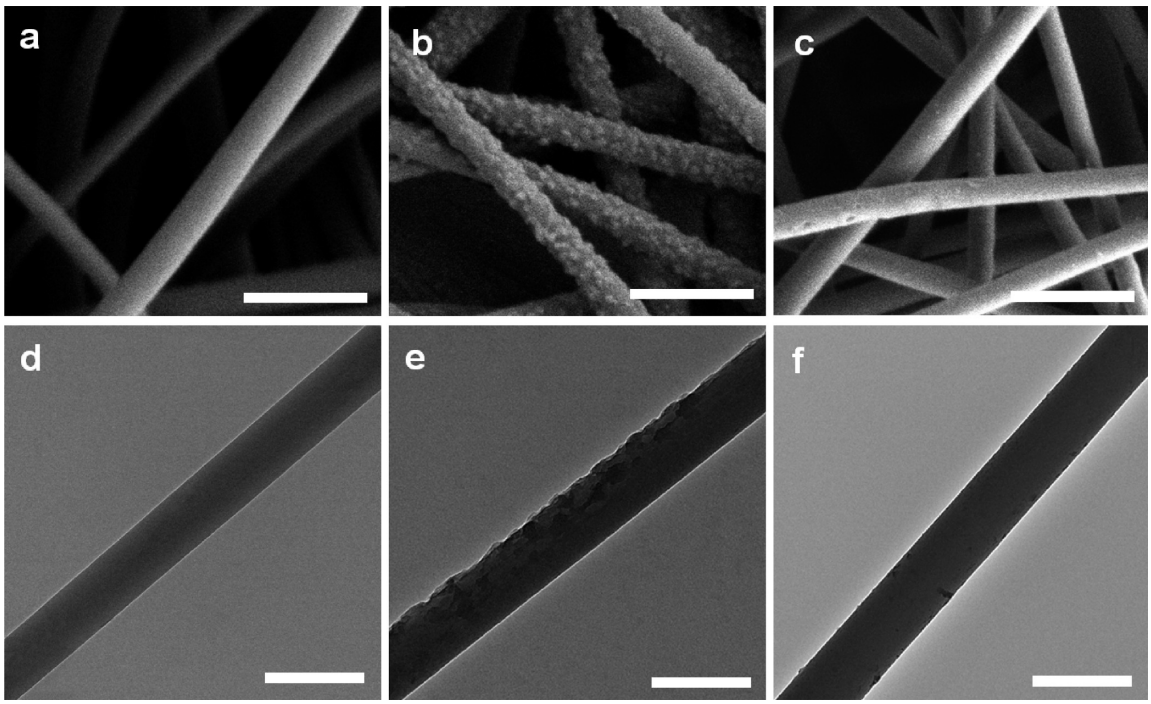

Figure 4. (a−c) SEM and (d−f) TEM micrographs of PAN nanofibers (a,d) uncoated, and coated with (b,e) PPy or (c,f) PEDOT. SEM scale bars represent 1 μm; TEM scale bars represent 500 nm.

vapor-phase polymerization most probably occurred primarily at the surface of the mat and the observed filmlike polymer coating probably formed rapidly at the surface, acting as a physical barrier to the monomer vapors, preventing an efficient polymerization within the mat. Upon rinsing with methanol, the unreacted oxidant was removed, partially restoring the porosity of the internal part of the mats.

By decreasing the FeTos solution concentration to 20 wt %, the viscosity of the solution was reduced, allowing the solution to coat the individual fibers, without filling the entire porosity, as can be seen in Figures 3b,e. After polymerization, thin films were still visible at the intersection of some fibers, but the open porosity of the mats was globally preserved. Decreasing further the oxidant concentration down to 13 wt % ensured the deposition of an ultrathin coating on the nanofibers without the formation of films between the fibers, and preserving the entire porosity of the mats (cf. Figures 3c,f). The porosity was then only decreased by 1 or 2%.

PAN nanofibers presented a perfectly smooth surface with no asperities, as can be seen on Figures 4a and d. It is interesting to note the difference in the coating morphologies obtained with PPy and PEDOT. PPy produced uneven nodular coatings (cf. Figure 4b,e), whereas PEDOT coatings were very smooth and dense, hard to distinguish from the PAN substrate (see Figure 4c,f).

PAN fibers displayed a significant dispersity of diameters and therefore the diameter of over 80 nanofibers was measured at different locations of each sample in order to get reliable statistical trends and the most accurate estimation of the ICPs coating thicknesses. The average fiber diameters and standard deviations for all samples included in this study are summarized in Table 1. The average diameter of the uncoated PAN fibers was 280 ± 29 nm, which represents a typical distribution for electrospun fibers. Understanding the limitations of the measurement method, coating thicknesses were roughly estimated to be in the range of a few nanometers: from 5 nm for a PEDOT coating at an oxidant concentration of 13 wt % to 12 nm for a PPy coating prepared using a 20 wt % oxidant solution. Coatings were found to be thicker at higher oxidant concentrations, most likely because of the increase of the oxidant solution viscosity that produced thicker overlayers on the nanofibers. The rough and slightly porous PPy coatings were also found to be thicker than the compact and smooth PEDOT ones. According to our knowledge of the literature, these are the thinnest coatings of ICPs onto electrospun fibers that have ever been reported.

The fiber compositions, determined by the differences in the samples weight before and after coating, are presented in Table 1. The fibers coated with a 13 wt % oxidant concentration were composed of 90 wt % PAN and 10 wt % doped ICP, whereas at 20 wt % oxidant concentration, fibers with 80−85 wt % PAN and 15−20 wt % doped ICP were produced. Therefore, by controlling the concentration of the oxidant solution, it was possible to obtain ultrathin coatings of ICPs with minimal weight addition and preserving the entire porosity of the materials.

Structural Analysis. The crystallinity of the coated and noncoated nanofibers was studied by X-ray diffraction (XRD). The coatings were deposited using a 13 wt % FeTos solution, in order to ensure the characterization of the ICP coatings themselves and not the ICP thin films deposited between fibers (cf. Figure 3). Figure 5 shows the XRD patterns of coated and uncoated PAN nanofibers. Uncoated PAN nanofibers displayed a large peak at 17.2° followed by an amorphous tail at higher angles. This indicates that relatively high crystalline PAN nanofibers were produced, which is consistent with other studies previously published.[9,34] The small peak at 12.4° (also seen in the PAN+PEDOT pattern) is an artifact related to the glue used to hold the samples in the diffractometer chamber.

The PEDOT coatings showed some crystallinity (cf. Figure 5), with three characteristic peaks at 5.7, 11.7, and 24.9°. These peaks have been attributed to the (100), (200) and (020) reflections of the crystal lattice of PEDOT doped with tosylate anions.[35,36] PPy coatings were also found

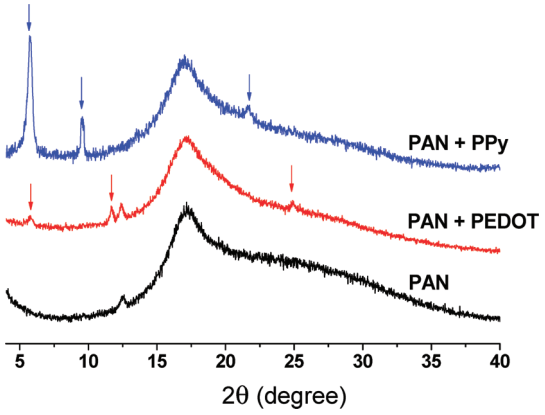

Figure 5. XRD patterns of the coated and uncoated electrospun mats.

crystalline, with characteristic peaks at 5.8, 9.8, and 21.7 degrees.[37,38] The crystallinity of the coatings was expected because the vapor-phase method is a solvent-free polymerization process where the tosylate anions produce a templating effect during the growth of the polymers. Thanks to that templating effect, particularly ordered polymers are generally obtained with this process.[39,40]

Conductive Properties. The electrical conductivity of the nanofibrous mats was tested using a four-point probe technique and the results are presented in Table 1. Significant conductivities were obtained for the coated nanofibrous mats: PEDOT-coated mats were measured to be 1 and 8 S/cm for oxidant concentrations of 13 and 20 wt % respectively, whereas conductivities of the PPy-coated mats were 0.07 and 0.10 S/cm at equivalent concentrations. The differences in the conductivities obtained for the two polymers were expected as PEDOT is known to be much more conductive than PPy. For example, VPP thin films of PEDOT have been reported with conductivities over 1000 S/cm,[31] whereas the highest conductivities reported for VPP thin films of PPy is 50 S/cm.[41]

These values, and especially the ones for the PEDOT-coated mats, are particularly high, considering the very low thicknesses of the coatings. For example, Gu et al. fabricated polyaniline-coated polyurethane nanofibers that displayed conductivities around 0.5 S/cm for an ICP coating thickness of 250 nm;[7] Zhu et al. obtained conductivities of 4×10^{-2} S/cm with PAN nanofibers covered with a 70 nm thick polyaniline layer.[5] Dong et al. reported the thinnest coatings (30 nm) of polyaniline on polymethyl methacrylate (PMMA) nanofibers, which showed a conductivity of 0.3 S/cm.[42] Previous work on PPy and PEDOT-coated nanofibers typically did not report conductivity data. In the present work, the best result was obtained with PEDOT coatings produced using an oxidant concentration of 20 wt %, which displayed conductivities around 8 S/cm for a 7 nm coating

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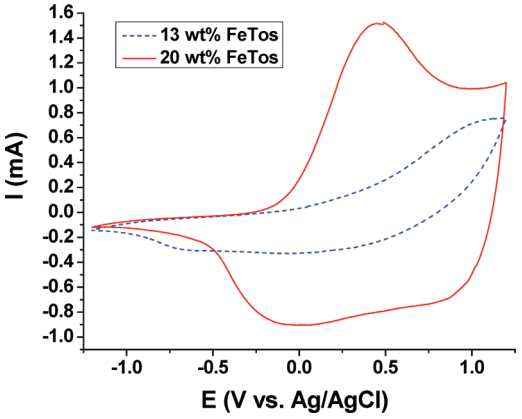

Figure 6. Cyclic voltammograms of PEDOT-coated mats at 10 mV/s in an organic electrolyte (NBu_4PF_6 0.1 M in acetonitrile). m_{PEDOT} = 0.62 and 0.96 mg for the 13 wt % and 20 wt % FeTos sol. mats, respectively. Dimensions of the mats 1 × 1 × 0.1 cm^3.

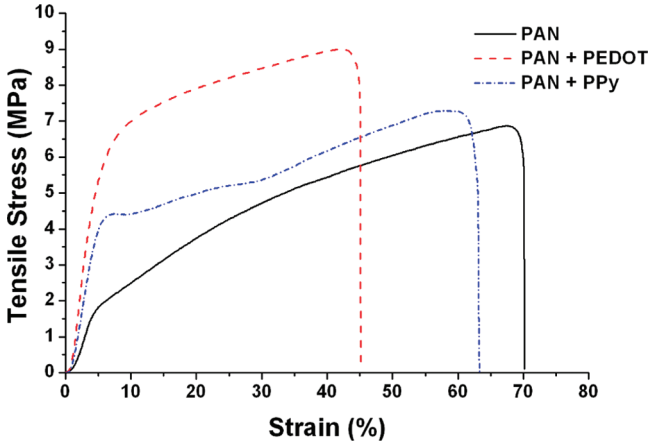

Figure 7. Typical strain−stress curves of uncoated and coated electrospun mats (13 wt % FeTos solution).

thickness. As discussed above, these high conductivities are believed to be related to the use of the vapor-phase polymerization process using FeTos as the oxidant, thanks to the templating effect.[40]

Finally, it is important to point out that the conductivity measurement technique used to determine the conductive properties of the samples assumes that the sample is not porous, which is obviously not the case of electrospun nanofiber mats. This means that the reported conductivity values represent the conductivity of the whole samples and not the conductivity of the coated nanofibers or the ICP coatings by themselves. These latter conductivities are believed to be much higher, as reported in the case of nonporous VPP deposited thin films.[31,41]

Electroactive Properties. The electroactivity of the coated mats was investigated using cyclic voltammetry in an organic medium (NBu_4PF_6 0.1 M in acetonitrile). The coated mats were connected using an alligator clip, without the use of an additional current collector. PPy-coated mats were not conductive enough to realize stable and reproducible electrochemical processes. On the other hand, PEDOT-coated mats displayed significant electroactivity, as can be observed in Figure 6. For the mats coated using a 13 wt % FeTos solution, the transport of the electric current in the mat was limited by its own conductivity (1 S/cm), as shown by the important peak-to-peak voltage (∼ 1.7 V). Consequently, an incomplete charge capacity of 25 mAh/g was obtained. The Coulombic reversibility of the doping/undoping process was 99%. By using a mat coated using a 20 wt % FeTos solution, the conductivity (8 S/cm) was high enough to efficiently transport the electric current through the mat. The oxidation and reduction peaks were well-defined, with low ohmic barrier to the charge transport, that caused the peak-to-peak voltage to decrease to ∼ 0.5 V. The charge storage capacity reached was 32 mAh/g with a 97% Coulombic reversibility, values important enough to envision applications in charge storage devices such as supercapacitors.[43] No signs of electroactivity degradation were observed after several tens of doping/undoping cycles.

Mechanical Properties. The coated mats presented no increase in the overall thickness after coating. They were fully bendable with no apparent delamination of the coatings. The coatings were strongly attached to the PAN substrate and did not detach even when the surface was rubbed with emery paper.

The mechanical properties of the nanofiber mats, uncoated as well as coated using the 13 wt % FeTos solution, were further investigated using strain−stress characterization (see Figure 7). As expected, the apparent Young modulus of the PAN nanofiber mats (52 ± 3 MPa) was increased after coating with the conducting polymers, the latter being known to be stiff polymers. The PPy-coated mats had an average Young modulus of 92 ± 7 MPa, whereas the PEDOT-coated mats reached the average value of 147 ± 13 MPa. The coatings also increased the tensile strength of the mats from 7.0 ± 0.5 MPa for PAN mats to 7.4 ± 0.4 MPa for PPy-caoted mats and 9.0 ± 0.8 MPa for PEDOT-coated mats.

Interestingly, a decrease in the elongation at break was also observed, from 70 ± 5% for the PAN mats to 62 ± 4% for PPy-coated mats and 43 ± 3% for PEDOT-coated mats. Usually, a coating layer that is stiffer than the substrate causes an increase of the Young modulus of the overall material, as observed in the present experiments, but does not decrease the stretchability of the substrate. What is rather observed is a cracking of the stiffer coating when the extension becomes too high, followed by the normal elongation of the substrate. The fact that the elongation at break is being decreased upon coating shows that the chemical structure of the PAN nanofibers is somehow affected by the coating process. Two hypotheses can explain this phenomenon: (1) an attack of the PAN nanofibers by the oxidant during the first part of the coating process, and (2) a partial interdiffusion of PPy/PEDOT chains and PAN chains at their interface. To verify the first hypothesis, we carried out several control experiments: the PAN nanofiber mats were subjected to the same coating procedures, but without the polymerization step. In another set of control experiments,

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the FeTos-coatings were kept 1 day on the mats before rinsing, to maximize a potential effect of the oxidant on the PAN chains. After rinsing with methanol, the FeTos layers were entirely dissolved and the mats overall properties were found similar to the pristine PAN mats, showing that the FeTos oxidant was not reacting with the PAN nanofibers. Therefore, it must be concluded that the modifications of the mechanical properties of the mats upon coating shall come from a partial interdiffusion of the conducting polymer chains with the PAN chains, stiffening the overall composite material and decreasing its stretchability.

Besides, the conductivities of the mats were barely affected by the stretching process: they were measured at 0.8 ± 0.2 S/cm at 40% elongation for PEDOT-coated mats, and 0.045 ± 0.01 S/cm at 55% elongation for PPy-coated mats (compared to 1.0 and 0.07 S/cm, respectively). This result is a further demonstration of the excellent adhesion of the coatings to the PAN nanofibers.

Conclusions

Flexible and ultraporous conductive nanofibrous materials were obtained by coating PPy or PEDOT onto electrospun polyacrylonitrile (PAN) nanofiber mats. A two-step vapor-phase coating process was used in order to obtain ultrathin and well-ordered films. The concentration of the oxidant solution was found to be a key parameter in order to preserve the open porosity of the nanofibrous mats. Coating thicknesses varied from 5 to 12 nm depending on the polymer and oxidant concentrations. The polymerization time and temperatures were very different according to the monomer used: pyrrole polymerized at ambient temperature within a few minutes whereas more than one hour at a temperature of 60 °C was necessary to polymerize EDOT. The coatings presented some crystallinity and high conductivities, probably because of the templating effect of the tosylate anion during the polymerization. In particular, PEDOT-coated PAN nanofibers showed conductivities in the range of 1−10 S/cm. Their electroactivity, obtained without the need of an additionnal current collector, showed promising results and could find applications in conductive textiles, sensors,[6,27] biomedical devices,[30,44] or energy storage devices.[8,43] Finally, the study of the mechanical properties of the coated mats demonstrated a very good adhesion of the coatings to the PAN nanofibers, possibly because of a partial interdiffusion of the polymer chains at the interface. Moreover, the conductivity showed almost no decrease upon stretching.

Acknowledgment. The authors thank Karine Théberge from NRC-IMI for the SEM and XRD analysis.

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