Development of conductive polymeric fibers for flexible electronics applications

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ABSTRACT

Conductive micro and nanofibers have been produced by melt-spinning and electrospinning. Melt-spinning uses mechanical forces to stretch fibers while electrospinning allows the production of fibers using the force of an electric field to stretch them. Alternatively, textile multifilament fibers were coated with intrinsically conducting polymers (ICPs). The fibers were characterized by electron microscopy (SEM, TEM) as well as 4-point probe conductivity measurements.

Keywords: Conductive fibers, melt-spinning, electrospinning, conductive coatings, conducting polymers, carbon nanotubes, nanocomposites.

1. INTRODUCTION

An increasing number of functionnalities are being integrated into soldiers' garments, from GPS antennas, to communication modules, sensors, etc ... The need to efficiently integrate all these electronic devices into textiles has become a key issue for the development of future soldiers wearable equipment. Flexible and lightweight electronic devices, such as the lighting panels of Crosslink[1] or the photovoltaic devices from Konarka[2], represent very promising approaches. However, the connections between the devices are still made of stiff and heavy metal wires that hinder an all flexible integrated approach. Therefore, there is a real need for the development of new polymeric and conductive fibers that could match the mechanical properties of common textile fibers, as well as keep the conductivity independent from mechanical (bending, stretching) and environment (oxidation, cleaning procedures, etc ...) stresses.

This paper describes several projects carried out at NRC-IMI that aim at the development of polymeric nano and microfibers which present electro-conductive properties. Fibers were obtained either by melt-spinning or electrospinning processes. The conductivity was obtained by adding carbon nanotubes (CNTs) into non-conductive polymers or by directly processing intrinsically conducting polymers (ICPs). In another approach, multifilament cotton yarns as well as nanofibrous non-woven mats were coated with ICPs. The fibers were characterized by microscopy techniques (SEM, TEM), and 4-point probe conductivity measurements.

2. RESULTS AND DISCUSSION

2.1 Melt-spinning of polymer-CNT composite fibers

Melt-spun conducting polymer fibers have a great potential of rapid market introduction, thanks to the already huge usage of melt-processes in the industry and hence the straightforward scale-up possibilities. Up to now, carbon-polymer conductive composites have not been able to be melt-spun into fibers because the high filler contents required to reach the conductive percolation levels (especially in stretched materials) are detrimental to the mechanical properties of the fibers. However, the use of carbon nanotubes can overcome this problem since CNTs have very high aspect ratios and, with adequate dispersion, electric percolation can be achieved even at very low contents in the polymer matrix.

Several polymer masterbatches containing multiwalled nanotubes (MWNTs) were studied. These masterbatches possess a high MWNTs content (~15 wt%) and conductivities in the range of 0.1 to 1 S/cm. However, when melt-processed as

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received, their mechanical properties were very poor, leading to brittle, non-usable fiber samples.

The masterbatches were then melt-diluted using the corresponding homopolymer. The conductivity of the composites was first measured on hot-pressed thin films and the results are presented in Figure 1. At 5 wt%, the conductivity decreased to 5.10^{-3} and 1.10^{-6} S/cm for PET and PA composites, respectively, while the conductivity of the PC composite remained high (0.16 S/cm). A heterogeneous dispersion of the masterbatch into the homopolymer, especially with PA composites, could explain this decrease in conductivity. At contents lower than 10 wt%, the mechanical properties of PA and PC composites improved significantly whereas the PET composites were still very brittle.

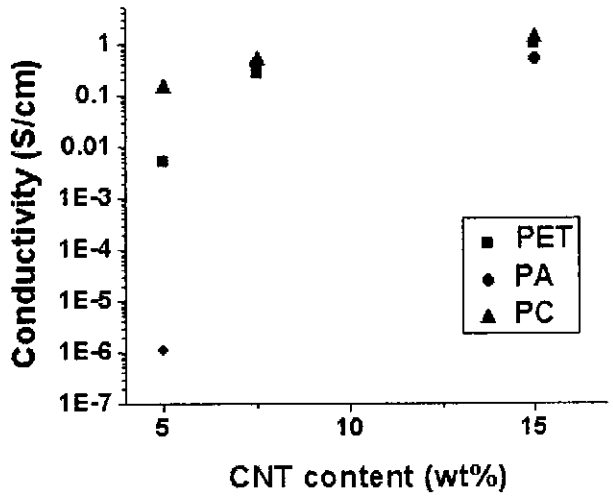

Fig. 1. Conductivity of polymer/MWNTs composite films. PET: polyethylene terephthalate; PA = polyamide 6,6; PC = polycarbonate.

The composites were melt-spun into single filaments, with minimal post-stretching, to yield conductive fibers having diameters around 500 µm (cf. Figure 2). Alternatively, coaxial multilayer fibers were produced in a one-step process.. Conductivities of the filaments were in the 10^{-2} S/cm range. Next steps will include the post-stretching of the fibers and the study of both mechanical properties and conductivity for varying fiber diameters and processing conditions.

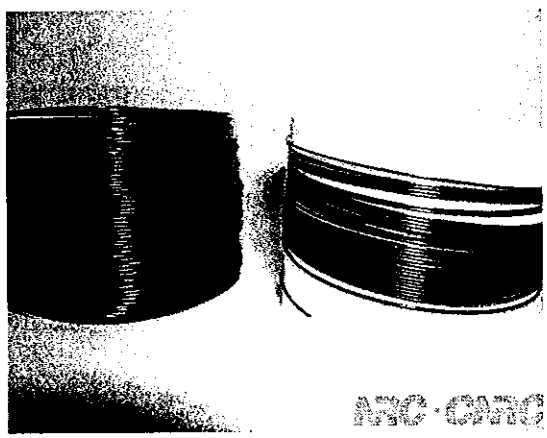

Fig. 2. Melt-spun nanocomposite monolayer filaments having a diameter ~ 500 µm.

2.2 Vapour-phase coatings of PEDOT on textile fibers

A straightforward method to obtain conductive fibers that can be integrated into textiles is to coat textile fibers with conducting layers. Conductive fibers top-coated with metal layers are already available on the market[3-4]. These fibers are lighter and more flexible than pure metal fibers and can be incorporated into textiles in an easier way. However, they cannot be stretched because of the stiffness of the metal. The metal coating can also delaminate from the textile fiber due to mechanical stress and oxidize in air with time, especially for silver coated fibers. Alternatively, coatings of intrinsically conductive polymers (ICPs) have also been deposited on textile fibers and showed promising results[5-6]. These coatings are much lighter than the metal coated fibers and can withstand higher deformations because of their all-polymeric nature.

An ICPs coating method was used to coat cotton and PET textile fibers. To ensure that the coating would not peel off due to friction, multifilament yarns were selected as substrates: the coatings on the internal sides of the fibers is then protected from the environment. To be able to coat the internal sides of the fibers, a vapour-phase coating procedure was used (cf. Fig. 3).Tthe fibers were first coated with an oxidant (iron p-toluenesulfonate) by dipping them in a basic alcohol solution containing the oxidant and a small amount of pyridine (ensuring the basicity of the solution), air-annealed to evaporate the solvent, and finally placed in a chemical reactor filled with the monomer vapours. In these experiments, the monomer selected was the 3,4-ethylenedioxythiophene (EDOT). Polymerization took place at the surface of the fibers, where the monomer vapours came into contact with the oxidant, resulting in a very thin layer of conducting PEDOT at the surface of the fibers both on the external and internal sides of the fibers.

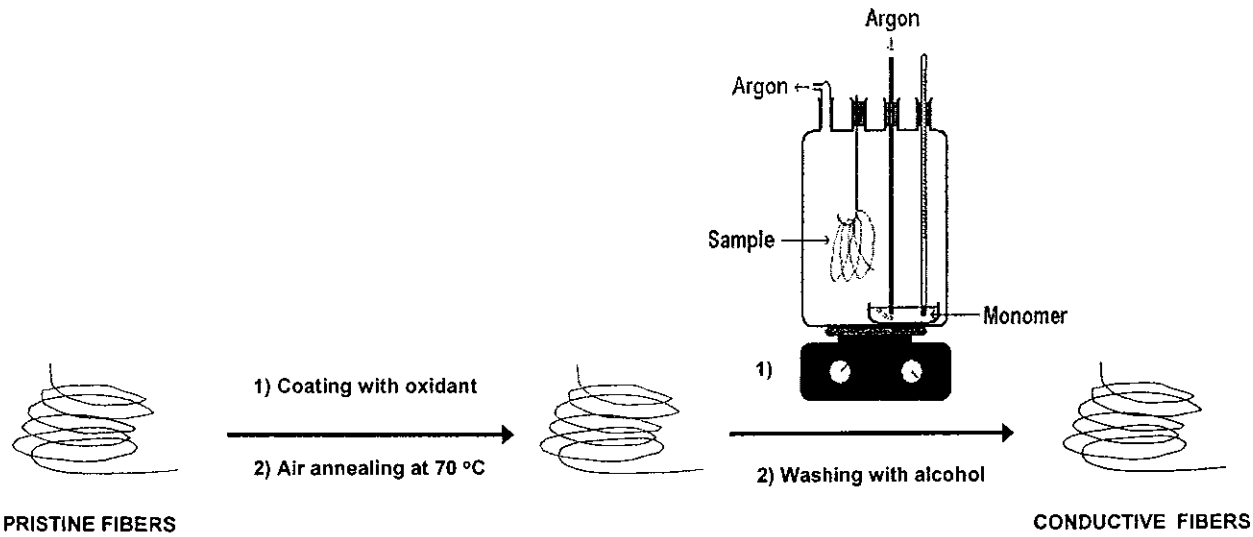

Fig. 3. Scheme of the multifilament vapour-phase coating procedure.

SEM studies revealed that the coating was present at the surface of the fibers as well as between the fibers (cf. Fig 4). The coatings presented a good resistance to abrasion and did not affect the mechanical properties of the fibers. The coated yarns presented the blue colour characteristic of PEDOT (cf. Fig. 4e). The 4-points probe conductivity measurements of the yarns gave results as high as 10 S/cm, with a remarkable stability over time. During the polymerization, the oxidant anion played the role of dopant to the polymer, ensuring a stable doping form even after rinsing and drying of the yarns. These conductive fibers could be easily integrated into textiles by weaving or embroidery techniques.

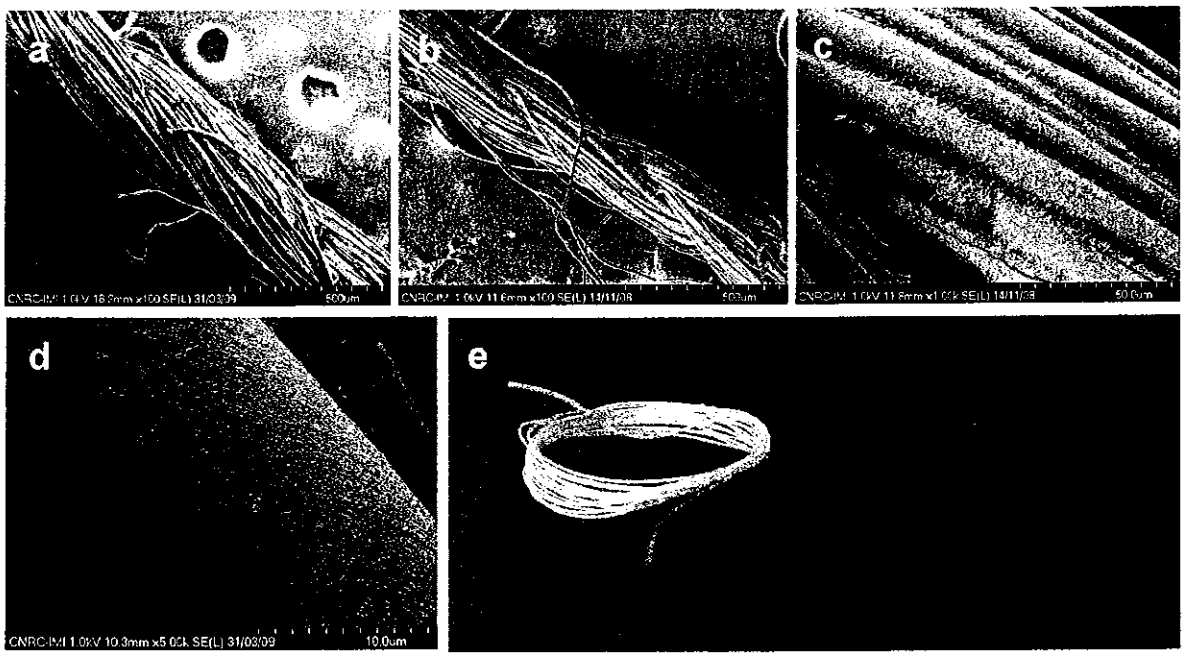

Fig. 4. (a-d): SEM images of uncoated (a) and coated (b-d) multifilament yarns of PET (a-c) and cotton (d). (e): photograph of uncoated (left, white) and coated (right, blue) cotton yarns.

2.3 Electrospinning of conductive poly(3-hexylthiophene) (P3HT) nanofibers

Electrospinning was used to obtain P3HT nanofiber mats[7]. Polyethylene oxide (PEO) with a molecular weight was added to the P3HT solution to assist the fiber formation during the electrospinning process. The fibers presented the bright red colour characteristic of P3HT (cf. Fig 5). Their average diameter was 500 nm. Conductivity of the nanofibrous mats doped with iodine vapours was measured according to the P3HT content and is presented in Fig. 5. The highest conductivities were obtained for P3HT contents higher than 75 wt% and were around 0.2 S/cm.

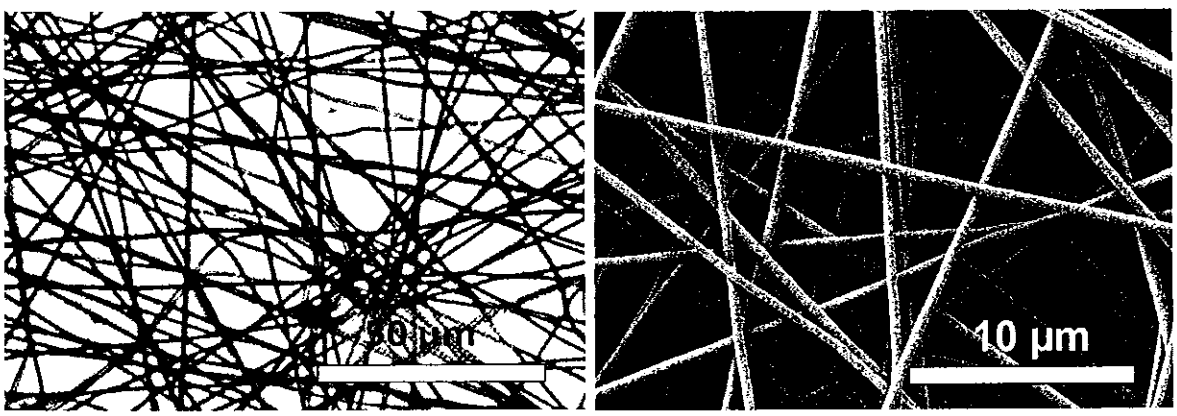

Fig. 5. Optical microscopy (left) and SEM (right) images of P3HT-PEO nanofibers obtained by electrospinning.

It was possible to increase the conductivity of the mats by an order of magnitude (up to 2.7 S/cm) by using a more regioregular polymer, synthesized with the Rieke method instead of the regio-irregular polymer previously used (polymerized with $FeCl_3$). Regioregular polythiophenes are known to be much more conductive than their irregular counterparts, explaining the observed increase in conductivity. Another way to increase the conductivity was to align the

fibers during the electrospinning experiments by using a rotating drum collector. A significant increase of the conductivity measured in the fiber alignment direction was observed for both regioirregular and regioregular polymer mats , (up to 0.3 S/cm and 6.7 S/cm, respectively).

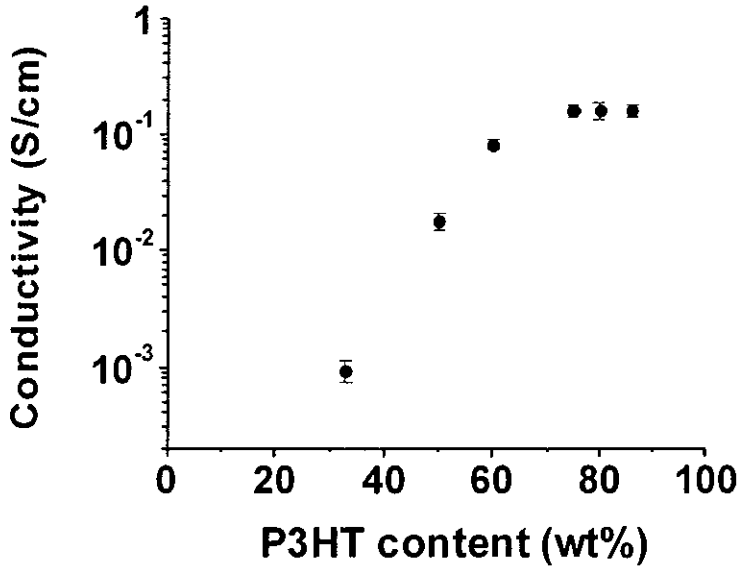

Fig. 6. Conductivity of the nanofiber mats at different P3HT content in the fibers.

These conductive nanofiber mats are promising for flexible electronic applications such as wearable sensors, by taking advantage of the high surface area developed by these nanofiber mats, combined to the resistive sensing properties of the ICPs to a variety of chemical vapours[8].

2.4 Vapour-phase coatings of ICPs onto polyacrylonitrile electrospun nanofibers

The vapour-phase coating procedure developed to coat textile multifilament yarns was used to coat electrospun nanofibers with conducting polymer layers[9]. Polyacrylonitrile (PAN) was chosen as substrate because of its very stable electrospinning process that allows the easy continuous production of nanofibers. The same oxidant solution was used as in the yarn coating experiments (cf. 2.2). Both PEDOT and polypyrrole (PPy) were coated on the PAN nanofiber mats and pictures of the resulting mats are shown in Figure 7.

The concentration/viscosity of the oxidant solution was found to be critical to preserve the open porosity of the nanofiber mats: when the commercial solution (40 wt% of oxidant in butanol) was used, the viscosity was too high and the excess of oxidant could not be efficiently wiped off from the mat. Consequently, the ICPs polymerized as thick film structures and the non-woven porosity was lost (cf. Figs. 8a,d). By decreasing the oxidant concentration to 20 wt%, the viscosity of the solution was decreased enough for the solution to coat the individual fibers, as can be seen in Figs. 8b,e. However, thin films were still visible at the intersection of some fibers. Decreasing further the oxidant concentration down to 13 wt% ensured a coating of the nanofibers without the creation of films between fibers, then preserving the high porosity of the mats (cf. Figs. 8c,f).

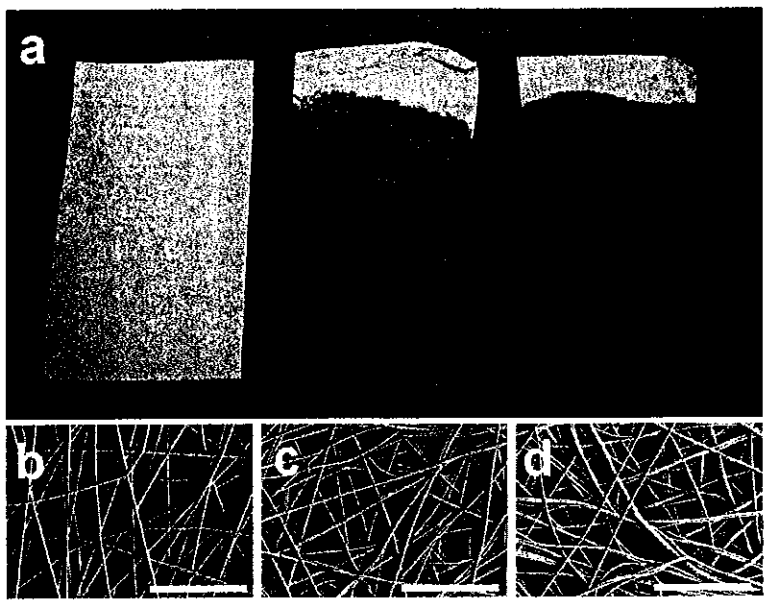

Fig. 7. Photographs (a) and SEM micrographs (b-d) of PAN nanofiber mats uncoated (a left, b) and coated with PEDOT (a middle, c) or PPy (a right, d) using 13 wt% oxidant solution. The mats are approximately 4 x 2.3 cm^2; SEM scale bars : 10 µm.

A statistical study of the fiber diameters was performed in order to estimate the coatings thicknesses. PEDOT layers showed an average thickness of 5 and 7 nm for 13 and 20 wt% oxidant concentrations, respectively, while PPy coatings were 10 and 12 nm thick at the same concentrations. PEDOT coatings were very smooth while PPy coatings were rough and uneven. As expected, conductivities were affected by the oxidant concentrations. PEDOT-coated mats showed conductivities of 1 and 8 S/cm for 13 and 20 wt% oxidant concentrations respectively. PPy-coated mats showed conductivities of 0.07 and 0.1 S/cm at corresponding concentrations. The mat conductivities were stable in time (no change observed after several weeks), the conducting polymers being doped by the tosylate anion during polymerization. These conductivities are in the same order of magnitude than the best ICPs electrospun nanofibrous mats reported in the literature.

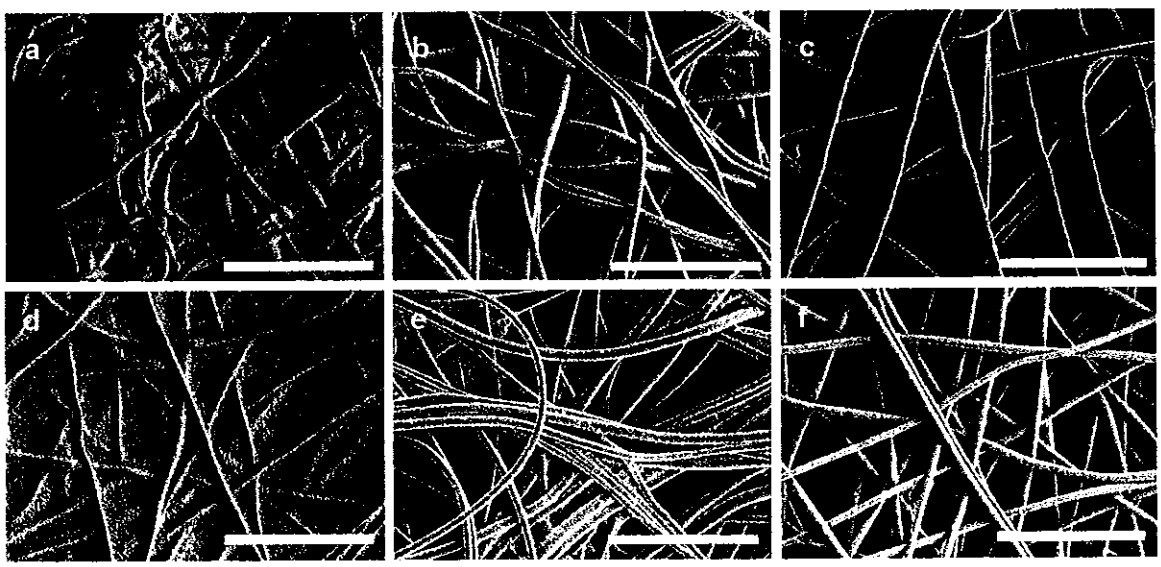

Fig. 8. PAN nanofibers coated with PEDOT (a-c) or PPy (d-f) using different oxidant solution concentrations: 40 wt% (a,d), 20 wt% (b,e), 13 wt% (c,f). Scale bars represent 5 µm.

The electrochemical characterization of PEDOT-coated nanofiber mats was investigated by cyclic voltammetry (cf. Fig 9). The coated mats were connected with an alligator clip, without the use of an additional current collector. PEDOT-coated mats displayed significant electroactivity. For a mat coated with a 20 wt% oxidant solution (red curve in Figure 9), the conductivity (8 S/cm) was high enough to efficiently transport the charges through the mat. The oxidation and reductive peaks were well defined, with low ohmic barrier to the charge transport. The charge storage capacity reached was 61 mAh/g with a 97 % coulombic reversibility. These results suggest that these structures could be useful in the fabrication of charge storage devices such as supercapacitors. However, the transport of charges in the mat coated with a 13wt% oxidant solution (blue curve in Figure 9) was limited by its own conductivity (1 S/cm). The ohmic barrier to the charge transport caused the peak-to-peak voltage to increase and the charge capacity to decrease to 25 mAh/g.

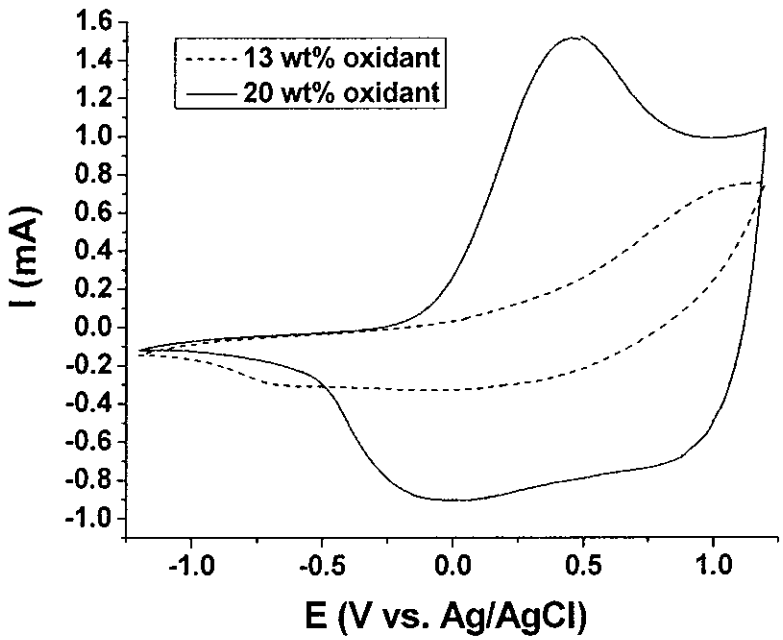

Fig. 9. Cyclic voltammograms of PEDOT-coated mats at 10 mV/s in an organic electrolyte (NBu_4PF_6 0.1M in acetonitrile). Dimensions of the mats : 1 x 1 x 0.1 cm.

3. CONCLUSIONS

Several techniques were used to produce non-metallic conductive fibers. Melt-spinning of CNTs nanocomposite fibers were produced using an industrial extrusion technique that could be easily scaled-up to produce conducting fibers for a number of applications, including data and energy transmission into textiles, as well as resistive heating textiles. Alternatively, a vapour-phase coating procedure was developed to produce multifilament textile yarns, with promising properties: high conductivities and no observable impact on the mechanical properties of the fibers. Integration of these fibers into textiles is envisioned, for data and energy transmission purposes. Finally, nanofibrous conductive non-woven mats were produced by electrospinning. Potential applications for these highly porous, ultra-lightweight and flexible materials include wearable sensors and flexible energy storage devices.

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