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Fabrication of Highly Conductive PEDOT Nanofibers

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) nanofibers were obtained by the combination of electrospinning and vapour-phase polymerization. The fibers had diameters around 350 ± 60 nm, and were soldered at every intersection, ensuring superior dimensional stability of the mats. The nanofiber mats demonstrated very high conductivity (60 ± 10 S/cm, the highest value reported so far for polymer nanofibers) as well as very interesting electrochemical properties, due to the porous and nanostructured nature of the electrospun mats. The mats were incorporated into all-solid flexible supercapacitors that showed interesting performances for applications where flexible and lightweight energy storage devices are required.

INTRODUCTION

The development of nanofibers represents a research area of great interest due to the variety of potential applications of these structures. Electrospinning is one of the most commonly used techniques to obtain nanofibers because of its versatility and relative simplicity. In the past few years, an increasing number of studies have been dedicated to the fabrication of electrospun nanofibers containing intrinsically conductive polymers (ICPs) such as polyaniline, polypyrrole, polythiophenes or poly(p-phenylene vinylenes)¹. Potential applications of such nanofibers include conductive textiles, flexible organic electronics, energy storage and sensors. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most conductive and stable ICPs. In 2004, Winther-Jensen et al. reported the preparation of PEDOT ultrathin films showing conductivities exceeding 10^3 S/cm using a vapour-phase polymerization process². However, much lower conductivities, in the order of 10^{-4} to 1 S/cm, have been reported for electrospun fibers incorporating PEDOT^{3,4}. Conductivities in the order of 10 S/cm were also observed on PEDOT nanofiber webs but the fiber geometry was not preserved and the webs were transformed into a porous film structure upon rinsing procedures⁵.

The authors have previously reported on the fabrication of pure PEDOT nanofibers using a two-step process combining electrospinning and vapour-phase polymerization. The first results led to highly conductive porous materials (200 S/cm) but the fibers partially "melted" in the process⁶. In this paper, we describe the optimization of this technique. Well defined and highly conductive nanofibers of pure PEDOT have been successfully fabricated. The structure and morphology of the nanofibers were characterized as well as their spectroscopic and electrochemical properties. Finally, flexible all-solid supercapacitors were built using these PEDOT nanofibers and characterized as flexible energy storage materials.

EXPERIMENTS

PEDOT nanofibers were obtained using a two-steps procedure. First, to a solution of iron tosylate (FeTos) 40wt% (Clevios CB40 from HC Starck, Inc.) was added 1 wt% of

polyvinylpyrrolidone (PVP; Aldrich; 1,300,000 g/mol) as carrier polymer and 2.6 wt% of pyridine (0.5:1 mole of FeTos). This solution was electrospun in a very dry environment (7-15 % relative humidity) using a conventional electrospinning equipment, at a flow rate of 0.5 ml/h and a voltage of 30 kV. The target was placed 15 cm away from the syringe needle tip. The resulting nanofibers were then placed in a closed reactor containing a small vial filled with the EDOT monomer. The reactor was placed under passive vacuum for five days. The monomer vapours polymerized, first at the surface and then in the bulk of the oxidant nanofibers. After polymerization, the nanofibers were rinsed with methanol and dried under active vacuum for 2 h.

The morphology of the nanofibers was characterized using scanning electron microscopy (SEM, Hitachi S4700). UV-Vis-NIR spectroscopy of the nanofibers was performed using a Perkin Elmer Lambda 950 spectrophotometer. Conductivity measurements were carried out using the four-point probe method. Electrochemical characterization was performed using a Biologic VMP3 multipotentiostat in an ionic liquid electrolyte (EMIBF₄). For 3-electrodes experiments, the reference electrode was Ag/AgCl NaCl saturated and the counter electrode, a platinum grid.

Flexible supercapacitors were built using PEDOT nanofiber mats as the active materials. Carbon cloths (Electrochem, Inc.) were used as current collectors and 100 µm thick sheets of polyacrylonitrile electrospun mats (average fiber diameter 280 nm, home-produced) were used as separators. In a first step, the supercapacitors were clipped between two Teflon plates and liquid EMIBF₄ was used as the electrolyte in a three-electrode configuration. In a second step, the supercapacitors were dried and then filled with a hot mixture of PVDF-co-HFP and EMIBF₄ (1:2). After cooling, the mixture formed a solid and flexible polymer electrolyte⁷.

RESULTS

Nanofibers fabrication process

PEDOT nanofibers were obtained according to a two-step procedure (cf. experimental section) and the fibers were characterized at each step. The oxidant nanofibers obtained at the first step contained a particularly low amount of carrier polymer (91.7 wt% FeTos; 2.3 wt% PVP and 6 wt% pyridine). Being mostly composed of a salt, the nanofibers were highly sensitive to any solvent vapours or moisture and liquefied quickly when exposed to an atmosphere with a relative humidity (RH) above 20 %. Consequently the electrospinning was performed under a controlled dry atmosphere (typically below 10 % RH). The nanofiber mats were then transferred to the vapour-phase reactor without contact with the room atmosphere and the polymerization reaction was immediately started.

In previous experiments, the vapour-phase reaction was performed under argon atmosphere⁶. However, there was a competition between the EDOT polymerization reaction (rendering the nanofibers insoluble) and melting of the oxidant nanofibers due to EDOT vapour absorption. This resulted in a partially melt fibers morphology. To circumvent the melting phenomenon, the kinetics of vapour absorption was decreased by placing the reactor under passive vacuum rather than placing it under argon atmosphere at ambient temperature. As the kinetic of polymerization was also significantly decreased, the polymerization time was increased from 2 h to 120 h (5 days). The reaction time effect was not observed on as-polymerized fibers, which always showed a nice "unmelted" morphology. However, after rinsing

the fibers with methanol to get rid of unreacted species as well as side-products of the polymerization, the fiber morphology changed radically (cf. Figure 1). At low polymerization times, the fibers "melted" during rinsing, whereas at high polymerization times, they kept their nanofiber morphologies.

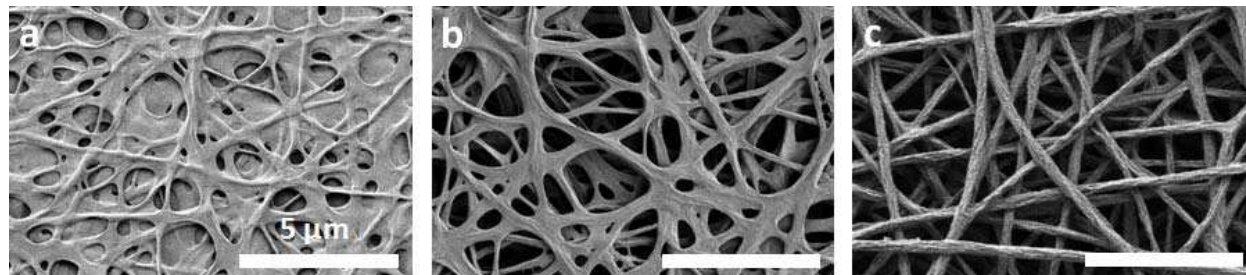


Figure 1: SEM images of methanol-rinsed PEDOT nanofibers obtained after 15 h (a), 60 h (b) or 120 h (c) of vapour-phase polymerization.

This phenomenon is believed to be due to the development of a core-sheath structure during polymerization, the EDOT vapours reaching and polymerizing at the surface of the fibers first and then diffusing inside the fibers. At low polymerization times, the PEDOT sheath layer was not strong enough and the whole structures collapsed during the rinsing step. The core of the nanofibers partially dissolved in methanol due to an excess of unreacted oxidant species. At higher polymerization times, the PEDOT layer was thicker, the amount of residual unreacted oxidant species was less and the structures could resist the rinsing procedure. However, a significant shrinkage phenomenon was still observed, as illustrated in Figure 2. The average diameter of the fibers was reduced from 710 ± 110 nm to 350 ± 60 nm.

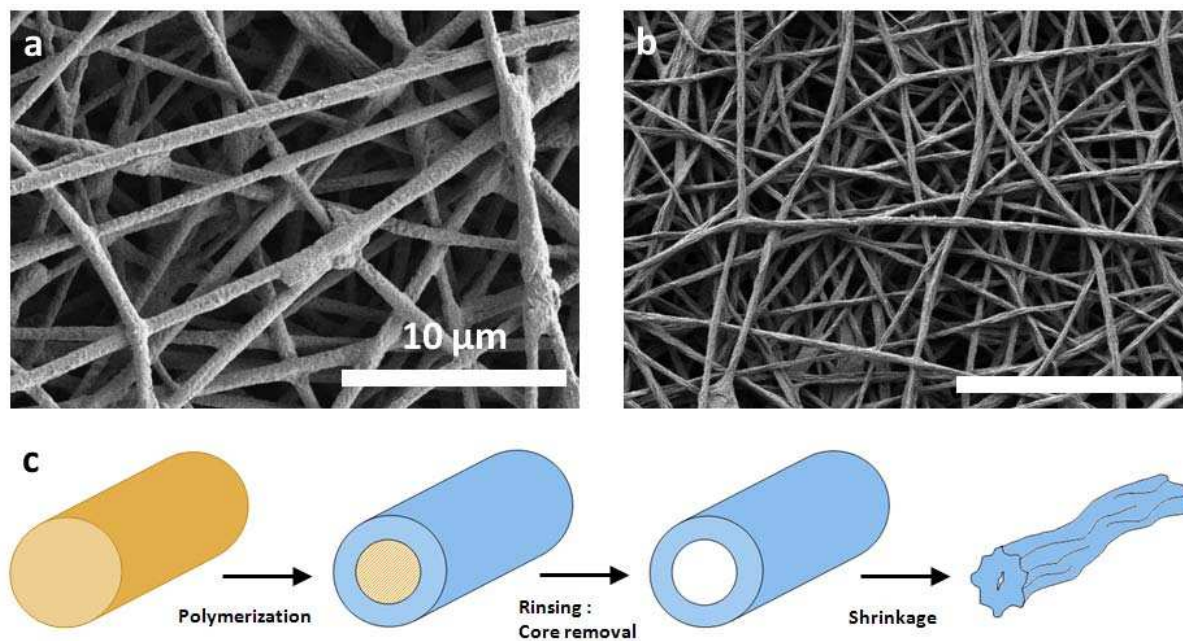


Figure 2: SEM images of nanofibers polymerized during 120 h, before (a) and after (b) rinsing with methanol. Scheme (c) illustrating the proposed process of the shrinkage phenomenon. Scale bars: 10 μ m.

Nanofibers characterization

The fibers were characterized by UV-Vis-NIR spectroscopy in order to investigate their electronic structure (cf. Figure 3). The characteristic PEDOT spectrum can be observed, with a low absorption in the visible and an increasing absorption after 700 nm, extending in the NIR region, which has been reported as a strong bipolaron absorption, indicating high level of doping⁸. The origin of the high absorption below 500 nm, uncharacteristic of PEDOT, is still under investigation.

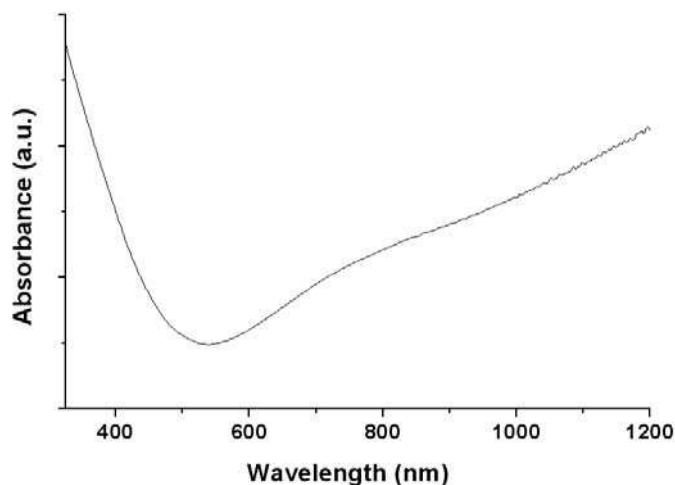


Figure 3: UV-Vis-NIR spectrum of the electrospun PEDOT nanofibers.

The conductivity of the nanofiber mats, measured using a four-point probe method, was around 60 ± 10 S/cm. To our knowledge, this is the highest level of conductivity for electrospun organic nanofiber mats reported to date. This high conductivity is believed to result from the use of the VPP process using FeTos as the oxidant, which is known to lead to highly crystalline and ordered polymers². Moreover, all the fibers were soldered at their intersections during the polymerization, ensuring perfect contact between the fibers and therefore a negligible ohmic barrier to the charge transport from one fiber to another. This soldering effect also provided a strong dimensional stability to the mats.

Besides, it is important to point out that the conductivity values obtained using the four-point probe technique are volume conductivities that do not take into account the materials porosity. Indeed, the mat porosity was estimated to 80 ± 5 % by simple weighting experiment, using a density of 1.6 g.cm^{-3} previously reported for tosylate-doped PEDOT⁹. By taking into account that the PEDOT nanofibers represent only ~ 20 % of the sample volume, it can be estimated that individual fibers should have conductivities around 300 S/cm, a value comparable with reported VPP-PEDOT thin films⁸.

The electrochemical characterization of the mats was performed under atmosphere conditions, without any special anhydrous or anaerobic condition. Figure 4 shows the cyclic voltammogram (CV) of a nanofiber mat at 5 mV/s. The high electronic conductivity of the nanofiber mat eliminated the need for any additional current collector and it was simply connected to a stainless steel alligator clip and dipped into the electrolyte. The peaks were very well defined, as can be observed on Fig. 4, confirming an efficient charge transport within the

mat as well as an easy insertion/desinsertion of doping ions within the active material. The charge storage capacity was 30 mAh/g with a 98 % coulombic reversibility.

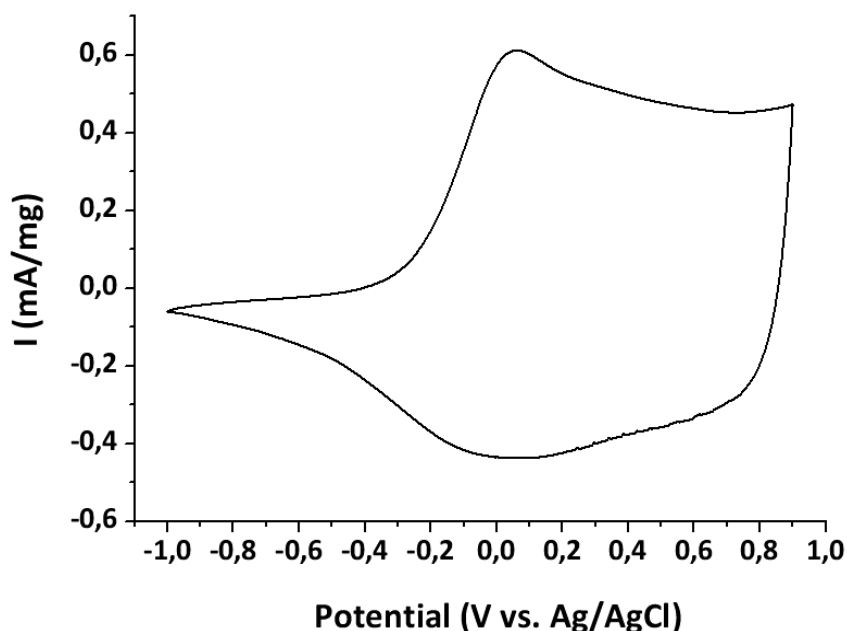


Figure 4: Cyclic voltammogram of a PEDOT nanofiber mat in EMIBF₄. Scan rate: 5 mV/s.

Application to supercapacitors

Flexible supercapacitors were built using the electrospun PEDOT nanofiber mats as both positive and negative electrodes. In order to ensure an efficient charge collection, flexible carbon fabrics were used as current collectors. The separator was made of home-produced polyacrylonitrile nanofiber mats.

In a first step, a three-electrode configuration was used in order to monitor the electrode potentials. Figure 5a shows the galvanostatic cycling curves of such a PEDOT/PEDOT cell. The cell voltage was controlled from 0 to 1 V. At 0 V, the electrodes were at 0.37 V/Ref. The PEDOT was then partially doped (see Fig. 4). By increasing the cell voltage, the positive electrode potential increased to 0.93 V/Ref (fully doped PEDOT) whereas the negative electrode potential decreased to -0.06 V/Ref (slightly doped PEDOT). The linear curves were typical of supercapacitors behavior with low ohmic loss at the interface of the active materials and the current collectors. The capacities obtained were 69 F/g for the positive electrode and 94 F/g for the negative electrode, showing that the PEDOT charge incorporation is less efficient at high doping levels (positive electrode case) rather than low doping levels (negative electrode case). At a current of 0.5 mA/cm², the cell capacity was 20 F/g (active materials mass), its energy 2.8 Wh/kg and power 230 W/kg.

In a second step, the supercapacitor stack was dried and the electrolyte replaced by a solid electrolyte (cf. experimental section). The supercapacitor was fully flexible and bending while performing had no effect on the performance. Figure 5b presents a typical galvanostatic cycling curve, using the same conditions as in the previous experiment (Fig. 5a). The cell capacity was 18.4 F/g, its energy 2.55 Wh/kg and power 230 W/kg (at a current of 0.5 mA/cm²),

demonstrating nearly no performance loss by replacing a liquid electrolyte by a solid one. By cycling at higher power (5 mA/cm^2), the power reached 2300 W/Kg but the energy was decreased to 1.3 Wh/kg . The cell performance in energy was decreased by only 4% after 1000 cycles, demonstrating a significant stability (cf. Fig 5b).

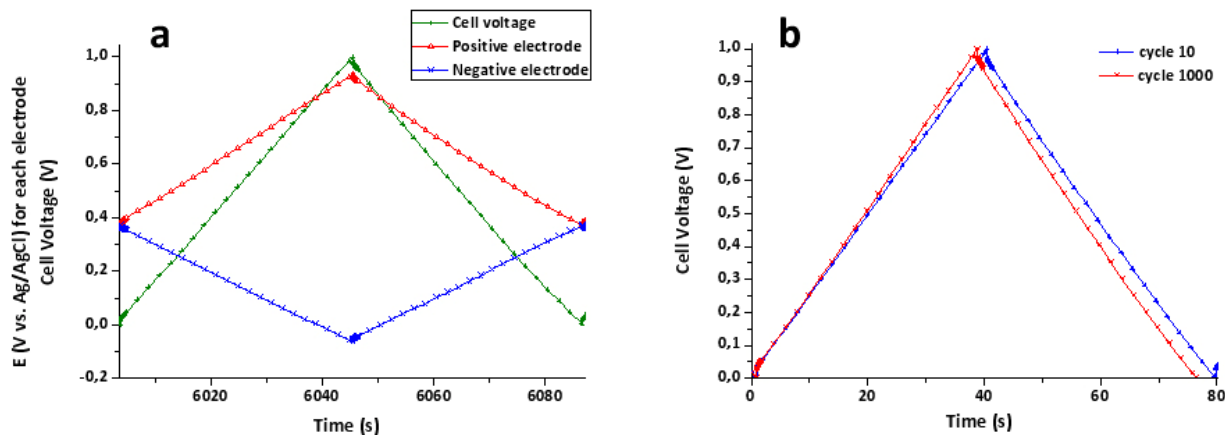


Figure 5: Charge/discharge galvanostatic cycling of a PEDOT nanofibers supercapacitor in an ionic liquid electrolyte (a) and in a solid electrolyte (b). Current = 0.5 mA/cm^2

CONCLUSIONS

PEDOT nanofibers were obtained by combining electrospinning and vapour-phase polymerization. The process parameters had to be carefully controlled at each step in order to avoid partial melting/collapsing of the fiber structures. The nanofiber mats demonstrated high conductivity ($60 \pm 10 \text{ S/cm}$) and improved electrochemical performances, due to their highly porous and nanostructured nature. These materials could find applications in a number of applications such as sensors, conductive textiles or energy storage.

Thin and flexible supercapacitors were built using PEDOT nanofibers and a solid ionic liquid electrolyte, which showed reasonable performances and high stability over cycling in ambient conditions.

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