ONE SIDE POLYANILINE COATED FIBERS BASED ACTUATOR

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In this study, one side aligned PANI coated micro-fibers were fabricated in order to develop a novel actuator configuration. Thus, electrospun PMMA fibers were coated only on one side with a thin gold layer guiding in this way the deposition of PANI (only on the side with gold considering an adequate PANI deposition time). Further, the half-metalized fibers were employed as working microelectrodes for electrochemical deposition of PANI. The prepared PANI coated fibers present actuation properties when they are in contact with an electrolyte like 1 M H_2SO_4. By switching the potential between +1.4 and -0.2 V, the fiber strips move due to the swelling/shrinking and anisotropic deposition of PANI film.

Keywords: polyaniline, fibers, actuator, artificial muscles, electrospinning, impedance measurements

1. Introduction

The interest in fabricating actuating micro-devices has been increasing in the past years as a consequence of high demand of biomimetic complex mechanisms such as tissue substitutes, implantable neuronal devices, animal-like robots, etc. [1-3]. In this context, conducting polymers (CP) are suitable candidates for such applications considering their biocompatibility, low actuation potentials and high mechanical properties [4,5]. The electroactivity of CP can be attributed to the doping/un-doping processes which occur when these materials are in contact with an ions source. Once the ions are moving inside and outside of

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the polymer chains, conformational changes and expansion/contraction of the entire structure is generated [6,7]. As well, the morphology of used structures plays an important role in the actuation process.

In particular, polyaniline (PANI) is frequently used for developing actuators due to the possibility of obtaining various shapes and morphologies which can improve the attributes of the final device. It was reported that the devices fabricated using PANI based porous membranes, micro-fibers or tubes exhibit enhanced properties than those based on classical films [8-10]. Therefore, the material morphology directly influences the actuation parameters by increasing the surface to volume ratio. As the active surface is higher, the more ions enter in the polymer structure and produce a macroscopic deformation. In a biomimetic approach, in order to get closer to the natural muscle (composed of skeletal muscular fibers made from myofibrils with the diameters of about 1-2 μm), the proposed actuator should be based on fibers.

The methods used so far for developing artificial muscles were taking into consideration only the coverage of thin metal layer, adhesive tapes with a CP film, as well the chemical synthesis of porous membranes. Gu *et al.* reported that the fabrication of a hybrid polyurethane/PANI parallel nanofibers with high specific area improves the incorporation of ions leading to high actuation strain. Parallel nanofibers form bundles, such configuration being very close to the natural muscular fibers structure [11].

Electrospinning is a technique usually employed for obtaining fibers with a wide range of diameters, highly defined shapes and functionalities [12,13] from different polymer precursors. However, electrospun PANI fibers are difficult prepared because PANI is very hard to be dissolved in biocompatible solvents, and its conductivity interferes with the electrospinning process. Therefore, for obtaining materials with improved properties and functionalities, several fabrication methods should be combined.

In the present work, the fabrication of a new actuator configuration by combining elecrospinning, sputtering metallization and electrochemical deposition of PANI is descried. Thus, aligned PMMA fibers by electrospinning a polymer solution in predetermined conditions were prepared. Such fibers collected on copper frames were coated on one side with a continuous gold layer in order to have a conductive surface of fibers and, in this way, the electrodeposition of PANI could be well controlled. Thus, one side metallized fibers were employed as working electrode for electrochemical deposition of PANI. The deposition was conducted in such way that the fibers were coated with a thin PANI layer only on the side with gold. The actuation performances of the obtained fibers were tested using 1 M H_2SO_4 as electrolyte. Thus, it was found that one side PANI coated fibers present an actuation time of about 5 s with the maximum displacement (0.1 cm), the applied potential required for

contraction/expansion are -0.2 and +1.4 V. Comparing with PANI completely covered fibers which show no movement due to the symmetrical volume changes, in this case, the asymmetric PANI film induces a displacement of the entire fiber strip.

2. Experimental

2.1. Materials

PMMA (M_W=350.000 g/mol) and N, N-dimethylformamide (≥ 99.8 %) were purchased from Sigma Aldrich. The precursors for synthesizing PANI, aniline (99+ %, Alfa Aesar) and sulfuric acid (95-97 %, Sigma Aldrich) were used without further purifications. All solutions were prepared using Millipore distillated water.

2.2. One side coated PANI fibers fabrication

Aligned electrospun PMMA fibers were prepared by using an in-house electrospinning setup equipped with an aluminum rotating drum collector with copper frames attached on it. The drum collector was rotated with a speed of about 2000 rpm. The spinneret consisted in a syringe needle through the polymer solution was fed with a rate of 0.5 ml/h by applying 20 kV. The precursor solution consisted in 10% (w/v) PMMA in N, N-dimethylformamide, and the collecting time was about 30 min.

Aligned PMMA fibers attached on copper frames were coated on one side with a gold layer by using DC magnetron sputtering. The metallized fibers were transferred on stainless steel frames in order to electrochemically deposit PANI. The polymerization procedure involves the use of the one side coated metallized fibers as working electrode, a platinum plate as counter electrode and a saturated calomel electrode (SCE) as reference. The precursor mixture was an aqueous solution composed of 0.05 M aniline and 1 M H_2SO_4. Consecutive chronoampetrometric pulses (with 0 V the lower limit and 1 V as upper limit), with a delay time of 0.5 s were applied in order to fabricate PANI thin layers. The deposition time was 65 s which was chosen in order to obtain the optimal PANI layer deposited on the gold covered side. The configuration of the resulting PANI coated fibers is presented in **Fig. 1(a)**. **Fig. 1(b)** shows the digital photo of the fiber strip coated with PANI with an uncovered segment which serves as contact.

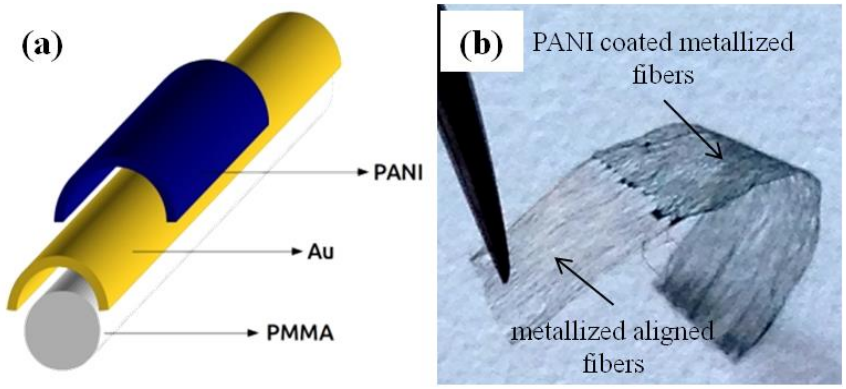

Fig. 1 (a) Schematic representation of the obtained fiber configuration and (b) digital photo of one side PANI coated fiber strip.

2.3. Characterization

The morphology of the one side PANI coated fibers was analyzed by Scanning Electron Microscopy (SEM) using a Zeiss Evo 50 XVP Scanning Electron Microscope while Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer Spotlight Spectrum 100 Spectrometer) was employed for the optical characterization of the samples in the wavelength range of 4000 – 500 cm^{-1}. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were also used for examining the electrochemical behavior of the aligned PANI coated fiber strips using 1 M H_2SO_4 aqueous solution as electrolyte. The actuation performances such as displacement, response time and applied potential to generate the movement were investigated. The samples used in actuation testes were approximately 2 cm in length (with the uncovered segments) with a width of about 0.2 cm.

All the electrochemical analyzes were performed using a three-electrode setup, where free standing one side PANI coated fiber strips were used as working electrode, a platinum plate as counter electrode and SCE as reference. The fiber strips were connected with the metallized segment to a platinum plate using silver paste. A computer controlled potentiostat (VoltaLab PGZ100) was employed for electrochemical tests. Only PANI coated sections have been immersed in the electrolyte. The EIS measurements were performed using the same electrochemical cell as in the case of actuation tests by applying different potentials (-0.2, 0, +0.2, +0.4, +0.6 and +0.8 V) in the frequency range 100 mHz-100 kHz, at 10 points per decade with 10 mV AC voltage amplitude. The experimental data were interpreted utilizing a ZView 2 Scriber Assoc fitting program.

3. Results and discussions

3.1. Morphological characterization

The fabrication of one side PANI coated fibers involves the combination of several preparation methods, hence the resulting fibres morphology was analyzed after each step.

Thus, in **Fig. 3(a, a')** and **3(b, b')** the SEM images of one side metallized PMMA fibers and PANI coated fibers (with a deposition time of 65 s) are presented. As it can be noticed, the gold layer is smooth, continous along PMMA fibers and have a thickness of about 100 nm. Compared with the gold layer, the PANI film presents some bumps, it is uniform deposited along the fibers and reaches an approximate thickness of 300 nm. The PANI deposition time was short enough in order to deposit PANI only on the fibers, avoiding the formation of a thick PANI embadded fibers film . Likewise, the fibers are well aligned, their diameter after PANI deposition hovering between 1 - 2 μm. The covering of the fibers only on one side was noticed by dissolving the PMMA cores in dichloromethane, and in the end some half microtubes were obtained.

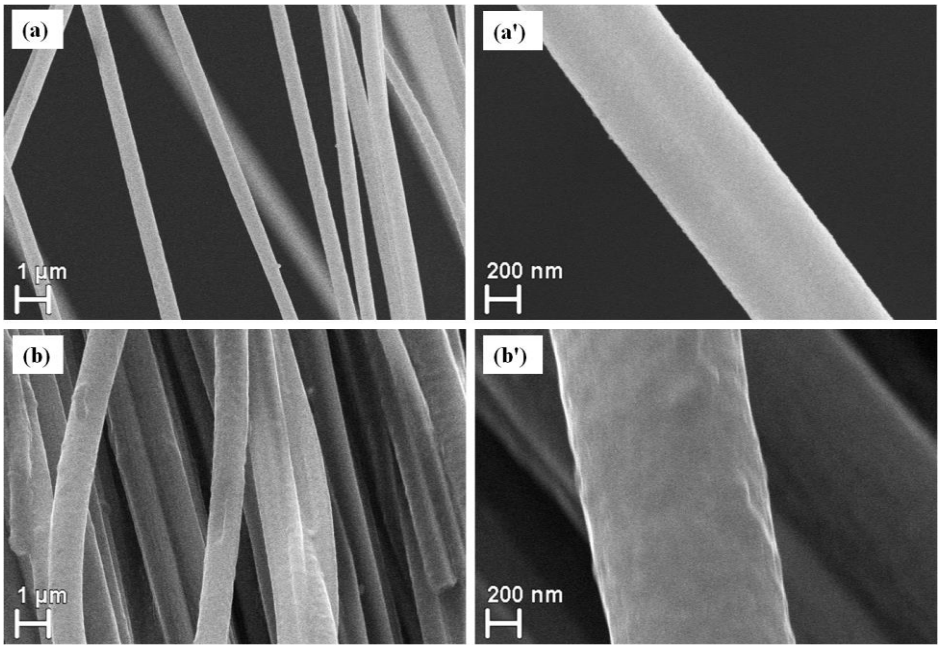

Fig. 2 SEM images of (a, a') the aligned gold coated PMMA fibers and (b, b') PANI covered metalized ones.

3.2. Structural analysis

After the PANI deposition process, the samples were rinsed with Millipore water and dried. Thus, FTIR spectrum of one side PANI coated fibers was registered in order to highlight the formation of PANI. Hence, in **Fig. 2**, the absorption bands typical for PANI can be identified. The absorption bands at 1558 and 1472 cm^{-1}, are assigned to C=C non-symmetric stretching vibrations in quinoid and benzenoid rings, having similar intensities revealing in this way the formation of emeralinde salt. Likewise, the bands at 1304 and 1238 cm^{-1} are related to C-N stretching vibrations of benzenoid ring. The absorption band at 806 cm^{-1} is characteristic to the out of plane bending vibration of C-H in the benzenoid ring.

The representative band at 1130 cm^{-1} is assigned to N=quinoid=N stretching vibrations. The polymerization of aniline takes place in the presence of sulfuric acid, consequently in the FTIR spectrum an absorption band at 1050 cm^{-1} assigned to the symmetric stretching vibrations of S=O can also be observed [14,15].

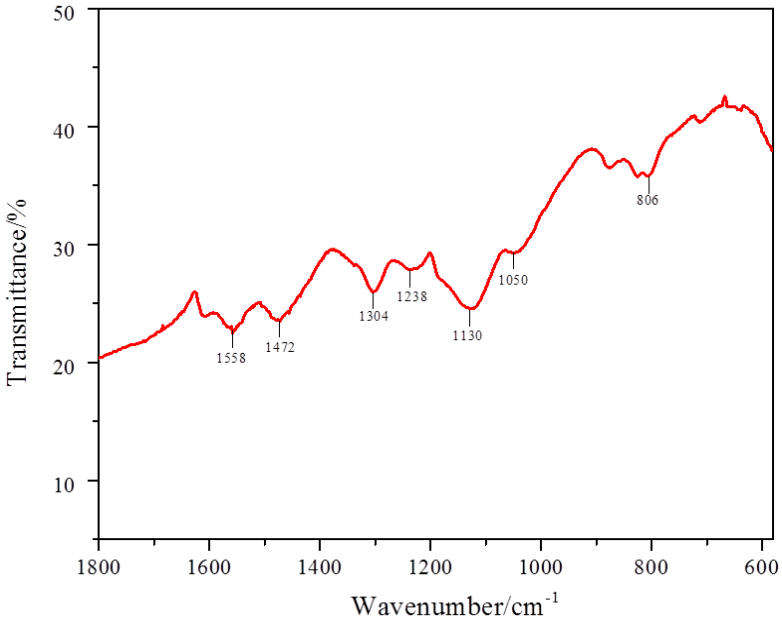

Fig. 3 FT-IR spectra of PANI deposited on gold coated PMMA fibers.

3.3. Electrochemical characterization

The CV of one side PANI coated fibers registered in 1 M H_2SO_4 at different scan rates is presented in **Fig. 4(a)**. As it can be noticed, the CV obtained by sweeping the potential between -0.2 and +1 V has three characteristic redox

pairs of peaks. According to the literature, the first pair of peaks appears (+0.2 and +0.1 V) due to the transition of leucoemeraldine to emeraldine salt, and second one (+0.6 and +0.8 V) is assigned the transition of emeraldine salt to pernigraniline. The third pair of peak (+0.5 and +0.55 V) could be associated with the formation of a PANI crosslinked structure or its partial degradation [16,17]. By increasing the scan rate, the cathodic and anodic peaks present slight shifts to more electropositive potentials and more electronegative potentials, this being a consequence of slow electron transfer processes in quasi or irreversible systems [18]. **Fig. 4(b)** shows the relation between the peak current (I) and scan rate (v) up to 250 mV/s, for the oxidation and reduction process. The obtained linear relation (the slope of PANI oxidation is 0.89379 ± 0.01893, and for reduction 0.69832 ± 0.03855) reveals that the oxidation/reduction is governed by combined adsorption and diffusion processes.

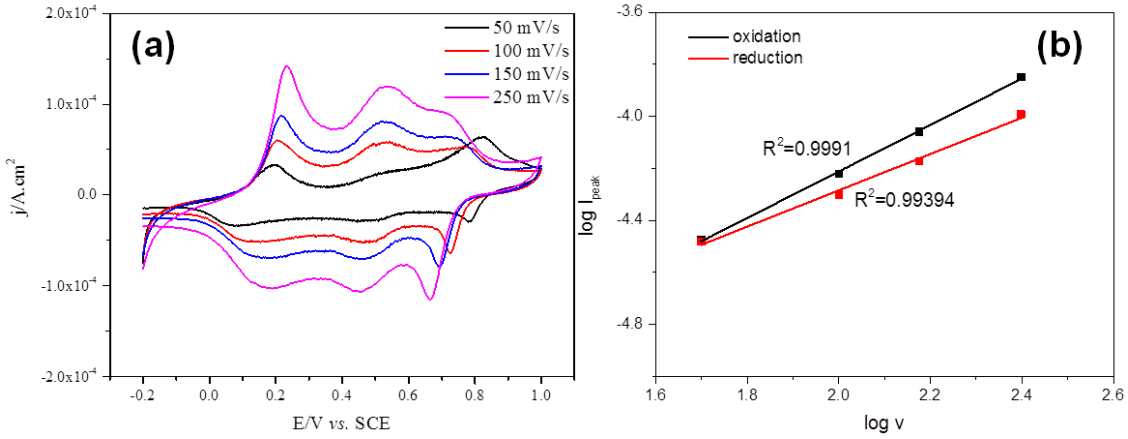

Fig. 4 (a) CV of PANI coated fibers at different scan rates, registered in 1 M H_2SO_4 and (b) the dependency of absolute values of peak currents on scan rate, R^2 is the correlation coefficient.

Further, for a better understanding of the actuation mechanism of one side PANI coated fiber meshes, impedance spectra using 1 M H_2SO_4 as ion source were recorded, by applying different potential for reducing and oxidizing PANI layer. The obtained results were analyzed considering a Randles electrical equivalent circuit consisting of an electrolyte resistance, a charge transfer resistance, one constant phase element which corresponds to the double layer capacitance of a rugged electrode and a Warburg element attributed to the diffusion processes.

Thus, in **Fig. 5a-f** the Nyquist plots (imaginary part, Z'' *vs.* real part, Z') are presented, both the experimental and fitted data. All the representations as a function of applied potential include a straight line in the low frequency range, followed by a semicircle which appears in the high frequency domain. The large

semicircle is assigned to a non-conductive PANI state, the electronic resistance of the polymer film being high. Once the potential is increased, the size of the semicircle is significantly shrinking, at +0.4 V reaching the lowest size, meaning that PANI is in conductive form at this potential, with a low charge transfer resistance. By increasing the applied potential, the characteristic semicircle is also increasing, reaching a high size at +0.8 V. The straight line which appears in all plots, has almost the same shape whatever potential is applied, which could correspond to a Warburg line associated with a semi-infinite diffusion for an electrode with an irregular surface and film thickness. It should be mentioned that no 90^o line correlated with a capacitive behavior was observed [19-21].

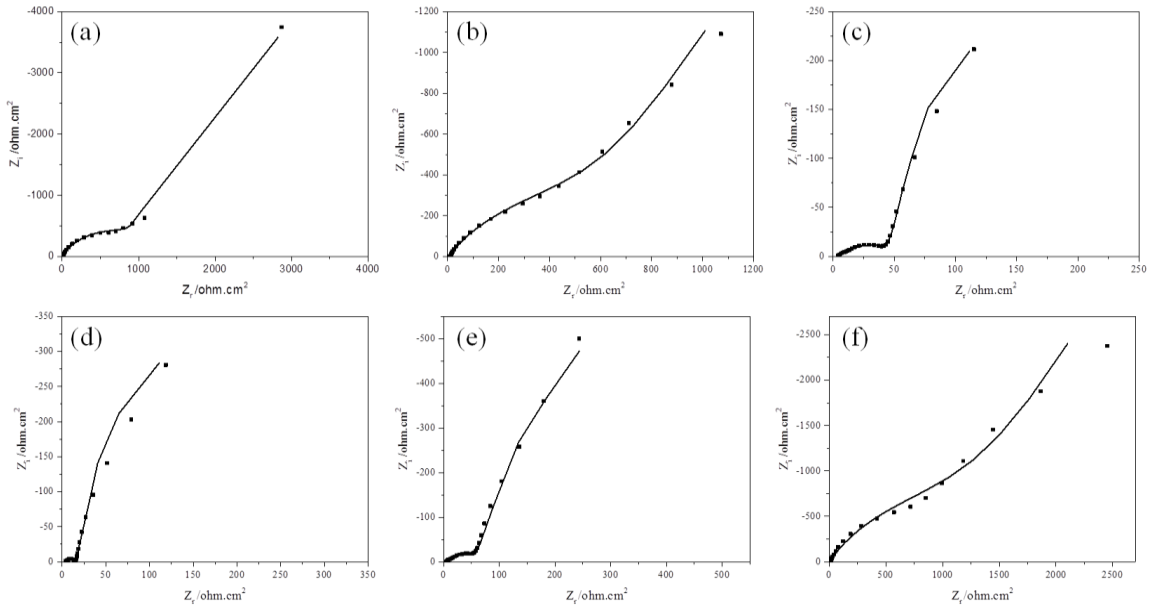

Fig. 5 Nyquist plots of one side PANI coated fibers measured at various applied potentials (vs. SCE) in 1 M H_2SO_4: (a) -0.2 V, (b) 0 V, (c) +0.2 V, (d) +0.4 V, (e) +0.6 V and (f) +0.8 V. Dots represent the experimental data and the lines indicate the fitting results.

3.4. Actuation tests

Regarding the displacement, strips of one side PANI coated fibers were analyzed using the same electrochemical cell as in the case of EIS and CV measurements. Thus, the electroactivity of the prepared actuator was demonstrated by applying periodic pulses, between +1.4 and -0.2 V. **Fig. 6(a)** presents the first 15 cycles (with a delay time of 5 s) corresponding to the movement of the fibers, showing a constant current during actuation, meaning that the actuator is stable over time. **Fig. 6(b)** displays the schematic representation of one side PANI coated fibers configuration and the actuation mechanism, figure

which is correlated with **Fig. 6(c, d, e)** in which digital photos of the fibers when the potential is switched between +1.4 and -0.2 V are presented. The fibers contract until reaching a final point and return to the initial position when the potential is switched to +1.4 V. The mechanism that describes the movement of PANI coated fibers is based on the migration of the electrolyte ions in/out of PANI film causing the swelling and shrinking of the electroactive layer, inducing the movement of the entire fiber [22,23]. Likewise, the deposition of the electroactive film only on one side has an important role in the fibers movement process because a full PANI coverage would be unable to promote a displacement due to the symmetric volume changes that occur during ions migration. Moreover, the distribution of the gold layer along the fibers provides a uniform propagation of the applied potential, making possible the movement of the fiber tips. In this case, the response time is in the range of few seconds with the maximum displacement. However, the displacement is relatively low (0.1 cm) maybe due to the PMMA fibers which cumber the structures. Removing the PMMA cores could enhance the displacement and decreases the actuation potential [24].

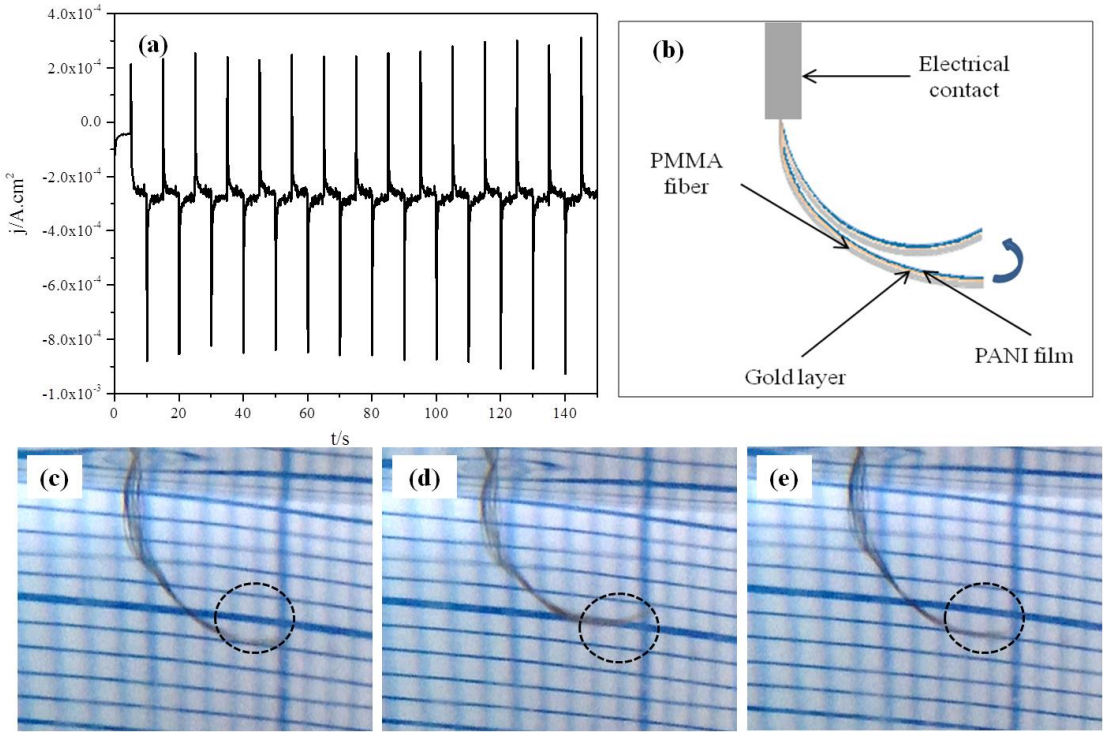

Fig. 6 (a) The first 15 cycles of one side PANI coated fibers recorded during actuation, in 1 M H_2SO_4 *vs.* SCE; (b) Schematic representation of fibers bending; (c, d, e) snapshots taken during actuation when the potential is switched between +1.4 V and -0.2 V.

Further, CVs of one side PANI coated fibers before and after 30 consecutive cycles were recorded and displayed in **Fig. 7(a, b)**. Thus, the applied potential was switched between +1.4 and -0.2 V, the pulse width was about 5 s, for 30 cycles, in 1 M H_2SO_4. It can be noticed that, after the actuation tests, the registered CV is changed, the PANI typical pairs of peaks are decreasing in intensity or are vanishing. Such behavior indicats a slight degradation of PANI due to the hydrolysis reaction (because the actuation tests are performed in aqueous solution) and due to an over-oxidation (the PANI coated fibers return to the initial position only by applying +1.4 V).

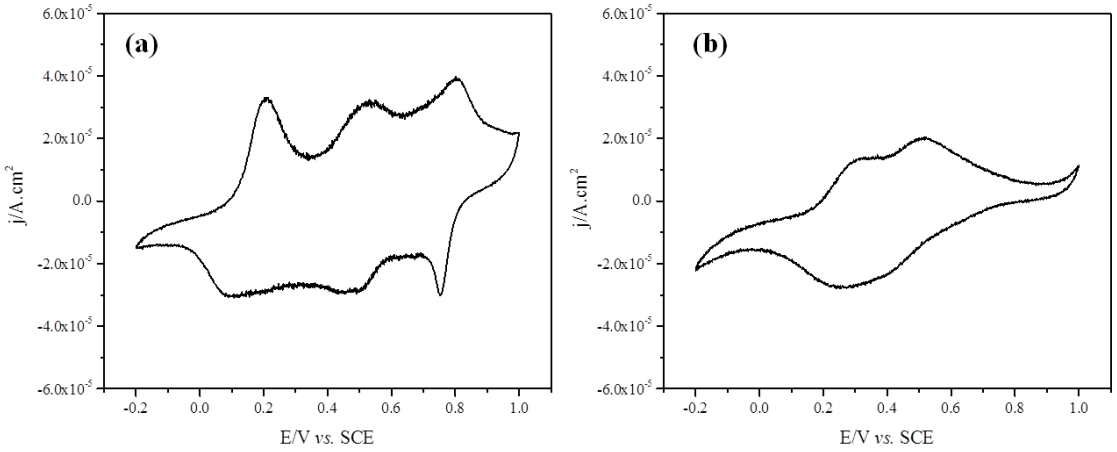

Fig. 7 CVs of one side PANI coated fibers (a) before and (b) after 30 applied cycles, at the sweep rate of 50 mV/s.

4. Conclusions

In the present work, a new actuator configuration based on one side PANI coated electrospun fibers was developed and tested using 1 M H_2SO_4 aqueous solution as electrolyte. The SEM images revealed a fibrous material made of well aligned fibers uniformly coated with an electroactive polymer layer. The deposition of gold only on one side of the fibers allows PANI to be deposited only on that side, inducing in this way an anisotropy in the actuator configuration which also has a contribution in the fibers bending (a complete coverage of the fibers does not induce any movement because of the generated symmetric volume changes).

The actuation performances of one side PANI coated fibers were investigated by applying consecutive pulses (with the upper limit of +1.4 V and lower limit of -0.2 V), revealing a bending motion generated by the swelling/shrinking of the PANI layer. In these conditions, the registered

displacement was of about 0.1 cm and the response time was in the range of few seconds (with the maximum displacement).

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R E F E R E N C E S

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