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Fibroin/Polyaniline microfibrous mat. Preparation and electrochemical characterization as reactive sensor

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ABSTRACT

A first time report on the reactive sensing capabilities of polyaniline (PANI) is presented. Microfibrous silk fibroin mats were coated with polyaniline (PANI) through in situ chemical polymerization. The mat gives closed coulovoltammetric responses in acidic aqueous solution, indicating that only reversible PANI oxidation/reduction reactions occur. Inside the reversible range the chronopotentiometric responses change with (sense) the reaction variables: electrolyte concentration, pH, temperature and driving current. The potential of the materials, or the consumed electrical energy, for a constant reaction time follow the linear or semilogarithmic relationships with each of the experimental variables predicted by the electrochemical kinetics. The reversible charge from the closed coulovoltammetric loop also senses the chemical or thermal energetic conditions of the reaction acting on the conformational movements getting deeper oxidation states for rising energetic working conditions.

1. Introduction

Conducting polymers are soft and wet reactive dense gels whose composition mimics the intracellular matrix (ICM) of functional biological cells [1] including reactive biopolymer chains, ions and water. The gel reactions (oxidation/reduction) shift the polymer gel composition and the related properties mimicking similar functions from biological organs. Devices driven by those reactions (artificial muscles, smart membranes, batteries or electrochromic windows to mention just a few) [1] will sense any physical or chemical variable acting on the chemical equilibrium as stated by the Le Chatelier principle [2] or on the reaction rate as stated by the Otero's principle [3,4]. Several tools (one actuator and several sensors of the working conditions) work simultaneously in one multifunctional and physically uniform device derived from conducting polymers. The ensemble computer/power generator/artificial muscle (conducting polymer) can mimic the permanent feedback communication between brain and biological muscles [3,4]. The sensing ability of conducting polymers is originated from their reactive nature through the unique electrochemical reaction exchanging ions and water with the electrolyte, and extracting an electron from the polymer chain continuously at each step of the polymer reaction (oxidation and reduction).

This multifunctionality has been empirically studied and verified for different types of polypyrrole samples generated through chemical and electrochemical techniques using different types of dopants and electrolytes [3–10]. Very recently our group has proposed a physico-chemical self-consistent model describing, quantitatively, the dual sensing/actuating behaviors of conducting polymers and reactive materials [3,4]. The empirical study of polyaniline (PANI) and polyaniline derivative materials as a sensor of the working conditions during oxidation/reduction reaction, and therefore, suitable to drive any PANI based faradaic device, as far as we know, has not been reported yet.

PANI is a fascinating conducting polymer which has been studied extensively as a dry material having a constant composition in microelectronics [11], photonics [12], sensors [13], tissue engineering [14,15], electromagnetic interference shielding [16]; or as a reactive material whose properties change as a function of its composition in artificial muscles or actuators [17–23], fuel cells [24,25], supercapacitors [26], electrocatalysts [27], corrosion inhibition [28,29], rechargeable batteries [30], and so on. Depending on the oxidation state of polymer back bone PANI can exist in different forms, of which the completely reduced leucoemeraldine (LE), partially oxidized and partially reduced emeraldine salt (ES) and completely oxidized pernigranilne (PN) are the most prominent forms. This makes the chemistry of PANI a little bit different from other conducting polymers. Here we open the exploration of the

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new reactive sensing capabilities of PANI for the first time using a fibroin microfibrous mat coated with PANI obtained by chemical purification from silk cocoons and electrospinning of the attained solutions, followed by in situ chemical polymerization with aniline.

2. Experimental

2.1. Materials

Aniline (Fluka, purified by distillation under vacuum), Cocoons for Silk (obtained from IMIDA), Ammonium persulfate (APS, Fluka), Methane sulfonic acid (MSA, Sigma-Aldrich), Ethanol (Panreac), Lithium Bromide (Acros Organics, NJ), Hexafluoroisopropanol (HFIP, Sigma) were used as received. Ultra-pure water (obtained from Millipore Milli–Q equipment) was employed throughout the experiments.

2.2. Preparation of silk fibroin

Cocoons obtained from silkworms reared in the sericulture facilities of the IMIDA, were boiled twice for 45 min in 0.02 M Na_2CO_3 aqueous solution and then rinsed thoroughly with water to extract the glue like Silk fibroin (SF). The extracted SF was then dried at 40 °C for 24 h and dissolved in 9.3 M LiBr solution for 3 h at 60 °C to generate a 20% *w*/*v* solution. Then it was dialyzed in distilled water for 3 days and the resultant aqueous solution was freeze dried in order to have the purified silk SF ready to be dissolved in the desired concentration. Just before the experiment, a 17% *w*/*v* SF solution in HFIP was generated by dissolving the lyophilized SF during 24 h at room temperature.

2.3. Electrospinning: fabrication of the fibroin microfibrous mat

The silk microfibrous mat was prepared by electrospinning technique by adopting a similar procedure reported earlier [31]. The electrospinning setup used (Yflow™ 2.2.S-300 Electrospinner, Yflow, Spain) consists of a capillary tube with an inner diameter of 0.45 mm and an outer diameter of 0.80 mm, connected to a syringe pump (charged with 3 mL of SF solution in HFIP), two high voltage suppliers and a collector composed by a metallic surface covered with one piece of aluminum foil (10 × 10 cm). One of the high voltage suppliers is positively polarized and connected to the metallic tube where the polymer solution is projected; the other is negatively polarized and is connected to the metallic collector. The setup is grounded to avoid electric discharges to the users. For the electrospinning a voltage of +6 kV was applied to the capillary tube and −5 kV to the collector. The distance between the tip of the capillary tube and the collector was 10 cm and the injection rate of the polymer solution was 6 mL/h. After electrospinning, the mats were immersed in methanol for 10 min. In order to keep uniform meshes during drying, a low pressure was applied to the meshes employing filter paper in both sides of the meshes. Then they were washed in ultrapure water and stored at 4 °C.

2.4. Preparation of Silk Fibroin/PANI microfibrous mat

Silk Fibroin/PANI hybrid microfibrous mat was fabricated through in situ chemical polymerization of aniline in aqueous MSA medium using ammonium persulfate as oxidant at 5 °C by following a similar procedure reported earlier [32]. The silk microfibrous mat was suspended in a solution containing 0.005 mole of aniline dissolved in 50 mL of 1 M MSA for 2 hours at 5 °C. A solution of 0.0065 moles of APS dissolved in 50 mL of 1 M MSA was slowly added to the aniline solution containing the silk microfibrous mat at a rate of 2 mL/minute with gentle stirring. The polymerization reaction was carried out at a temperature of 10 °C for a period of 4 hours after which the reaction mixture was maintained at a temperature of 5 °C for further 18 hours. The microfibrous mat was taken out and washed with deionized water thoroughly and allowed to dry in air at room temperature. The singly coated fiber was again subjected to in situ polymerization in MSA medium under the same experimental conditions as explained above so as to form a second coating of PANI on the fiber surface. Two consecutive polymerizations were enough to ensure a uniform coating of the silk microfibrous mat getting good and reproducible electrochemical responses [33]. The as prepared polyaniline coated silk microfibrous mat (silk fibroin/PANI microfibrous mat) was taken out and washed thoroughly with deionized water and dried in air.

2.5. Characterization

A Nicolet 5700 Fourier transform infrared (FTIR) spectrometer (Thermo Electron Corporation) with smart orbit accessories (ATR technology) was used to record the reflective FTIR spectra of the microfiber. The microfibers were directly mounted on a diamond crystal platform of the spectrophotometer and the accessory allowed the focusing of the IR beam to a small area of the sample to record the spectra. Surface morphology of the fibers was examined using a scanning electron microscope (SEM, Hitachi S-3500, Japan). Electrical conductivity was measured by two point probe method using an Agilent 34410 multimeter at room temperature. Two metallic clamps were used to ensure the electrical contact and to keep the distance between them constant. Lengths were measured using a digital caliper (COMECTA, ±10 μm) and the thickness was measured using an electronic micrometer (±1 μm).

$$\sigma = I/E \times l/A \quad (1)$$

where I is the current, E is the potential, l the length of the microfibrous mat sample and A is the area of cross section of the sample.

Electrochemical studies such as cyclic voltammetry and chronopoterntiometry related to the sensing characteristics were performed using an Autolab electrochemical workstation (PGSTAT-100 potentiostat/galvanostat) attached with a personal computer and employing GPES electrochemical software. A sample of the PANI coated microfibrous mat of length 15.4 mm and 6.87 mm breadth and having a mass of 2.26 mg was employed to study the electrochemical responses. This sample was immersed in the electrolyte solution letting 5 mm outside the liquid surface to ensure proper electrical contact through a metal clamp keeping the clamp far from the electrolyte contact. The PANI mass was determined using a precision balance (Extend, Sartorius) weighing the dry mat before and after coating. The experiments were carried out in a three electrode electrochemical cell by using the silk fibroin/PANI microfibrous mat as the working electrode, an Ag/AgCl (3 M KCl) as the reference electrode and a stainless steel plate having a surface area of 4 cm^2 as the counter electrode using 1 M MSA aqueous solutions as the electrolyte. The working electrode was fabricated by attaching the silk fibroin/PANI microfibrous mat with a platinum wire using conductive carbon paste. A cryostat/thermostat (Julabo T25) with a precision of ±0.1 °C was employed to study the temperature influence on the electrochemical responses. Chronopotentiograms (CPs) as functions of concentration of MSA and applied current were recorded at an ambient temperature of 25 °C. Cyclic voltammograms (CV) are recorded by cycling the potential between -0.15 V and 0.80 V.

3. Results

3.1. FTIR analysis of the Silk fibroin/PANI mat

The FTIR spectrum of Silk/PANI microfibrous mats is shown in Fig. 1, showing characteristics peaks of PANI [32,34,35]. The