

Research paper

Polypyrrole coatings on gelatin fiber scaffolds: Material and electrochemical characterizations in organic and aqueous electrolyte



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ABSTRACT

Polypyrrole (PPy) was chemically deposited on glycose-crosslinked gelatin fiber scaffold (FS) by simple dip coating technique, resulting in conductive fiber scaffolds (CFS). The CFS samples were comparatively studied in aqueous and propylene carbonate solutions of equal concentrations of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) electrolyte. Our aim in this work was to characterize the mechanical and electrochemical properties of the CFS samples. The new CFS material was characterized by scanning electron microscopy (SEM) and FTIR measurements confirming chemical oxidized PPy deposits on FS. The electrochemical measurements applying cyclic voltammetric, chronoamperometric and chronopotentiometric measurements showed that while diffusion coefficients for both solvents were in similar range, the exchanged charge was nearly doubled in aqueous solutions. The specific capacitance of the CFS had the highest value in aqueous electrolyte reaching 175 F g^{-1} , which suggests that in addition to smart tissue engineering, this novel CFS material could also find application in energy storage.

1. Introduction

Chemically polymerized conducting polymers typically form particles [1] rather than uniform films, and in general those materials are used as electroactive materials [2], conductive composites [3], antioxidants [4,5], and sensors [6,7]. Fiber scaffolds of electrospun gelatin with a glucose additive have been found to be a promising biomaterial, as glucose concentration can be used to tune the extent of crosslinking and improve the mechanical properties as well as water stability of the resulting material [8,9]. Biomaterial fiber scaffolds consisting of randomly oriented fibers are ideal candidates for skeletal muscle tissue engineering [10–13]. Several natural-derived materials have been investigated in the past such as collagen [14] and gelatin [15] due to their excellent biocompatibility. Recent work of Peng et al. [16] highlighted the electrospinning methods achieving nanofibers applicable in tissue engineering, fuel cells, batteries, super capacitors and water treatment, the great challenges to address in the 21st century.

Nevertheless, the potential of conductive fiber material is not limited to biomedical uses only, as applications in electrodes [17],

supercapacitors [18] and sensors [19] have also been explored. There is a growing interest in stretchable conductive yarns in textile industries [20] and fiber materials for emerging wearable electronics [21]. However, solutions based on carbon nanotubes [22], graphene oxide [20] or the use of carbon fibers [21] has been the main focus, aiming at combining conductivity, foldability and tailorability, like in case of wearable supercapacitors [12].

Our goal in this work was to characterize the properties of the chemically deposited conductive coatings on glucose-crosslinked gelatin fiber scaffolds (CFS) in order to evaluate their applicability as electrode materials or (pseudo)capacitors. Conducting coatings based on PPy or PEDOT can be deposited on nearly any porous material by simple dip-coating in oxidant and monomer solutions, or vapor phase deposition [23].

Here we demonstrate that simple conductive coatings exhibit superior novel properties on soft biocompatible glycose-gelatin fibers with focus on their mechanical and electrochemical properties. We studied the charging/discharging properties of the material, as well as the diffusion coefficient in different solvents but same electrolyte

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(LiTFSI), as well as the specific capacitance at different frequencies 0.0025 Hz–0.1 Hz. The advantage of such bioactive and electroactive fibre scaffolds lays in the potential application in biochemical fuel cells [24], bio batteries [25] and smart patches [26], where simultaneous electroactivity and biocompatibility is required.

2. Experimental

2.1. Materials and methods

Propylene carbonate (PC, 99%), ethanol (technical grade) and ammonium persulfate (APS, 98%) were obtained from Sigma-Aldrich and used as supplied. Pyrrole (Py, 98%, Sigma-Aldrich) was vacuum-distilled prior use and stored at low temperature in the dark. Sodium dodecylbenzenesulfonate (NaDBS, technical grade) was acquired from Aldrich. Milli-Q water was used for solutions. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%) was purchased from Solvionic. Gelatin type A from porcine skin, D-(+)-glucose (99.5%), and glacial acetic acid (99%) were purchased from Sigma-Aldrich.

2.2. Electrospinning of fiber scaffolds

Glucose and Type A gelatin from porcine skin were used to prepare the solution for electrospinning. Glucose was mixed with gelatin in ratio of 1:10. The mixture was dissolved in 10 M acidic acid at room temperature during vigorous stirring on magnetic stirrer [7]. Fibrous scaffolds were prepared by electrospinning under the following condition: 5 ml syringe containing gelatin solution was pumped at speeds of 5–7 $\mu\text{l}/\text{min}$ at 17.5 kV. A New Era Pump Systems NE-511 was used as the syringe pump and a Heinzinger LNC 3000 for the high voltage power supply. Aluminum foil was used as the grounded target, placed 14.5 cm away from the syringe needle tip. Fibrous scaffolds were then removed from the foil and stored in Petri dishes until thermal treatment. Subsequent cross-linking was carried out by placing the fibrous scaffolds in an oven for 3 h at 175 $^{\circ}\text{C}$, in order to avoid gelatin degradation and to ensure proper cross-linking [9]. The fiber scaffolds had an estimated mean thickness of 16 μm .

2.3. Conductive coatings on fiber scaffolds

The fiber scaffolds were coated with PPy using APS (0.075 M) and NaDBS 0.01 M aqueous solution. 2 M pyrrole in 40% ethanol was applied as the monomer solution. The cross-linked fiber scaffold was first immersed in purified water, followed by soaking in monomer solution where it was gently stirred for about 30 s. After that the fiber scaffold was placed in APS/NaDBS aqueous solution, where it was kept around 20 s. Thereafter, it was put into ethanol solution where excess monomer was washed off, followed by purified water where excess APS and NaDBS were washed off. This procedure was repeated 4 times until PPy coating of sufficient thickness was achieved. The formation equation of PPy polymer with APS oxidant is shown elsewhere [5]. After polymerization, the material was stored in ethanol and dried using supercritical extraction with CO_2 .

2.4. Electrochemical characterization of conductive fiber scaffolds

The conductive fiber scaffolds were cut in 1 cm long, 1 mm wide strips with thickness of 48 μm . The weight of the fiber scaffold (FS) was found in range of $184 \pm 8 \mu\text{g}$ and the PPy coated scaffold in range of $428 \pm 28 \mu\text{g}$. The PPy coatings (dry state) had a weight of $244 \pm 13 \mu\text{g}$. In a three electrode set up with platinum counter electrode, Ag/AgCl wire (+320 mV vs. SHE) reference electrode, the conductive scaffold was fixed on a gold contact/electrode and electrochemical measurements were performed. Square wave potential and current steps at applied frequency 0.0025 Hz–0.1 Hz were made. The applied electrolyte was 0.2 M LiTFSI in water or propylene carbonate.

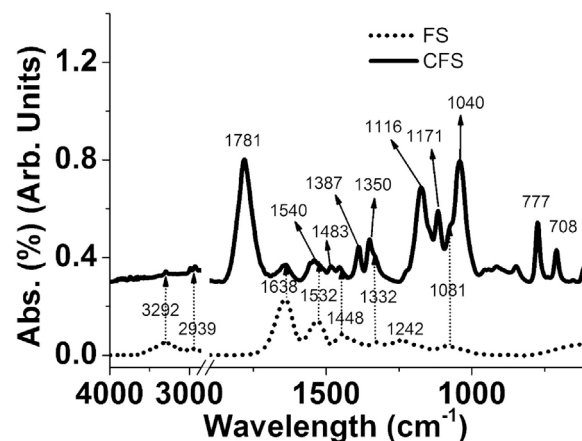


Fig. 1. FTIR spectra (4000–600 cm^{-1}) of FS (dotted) and CFS (solid line).

2.5. Other characterization

The CFS samples were characterized by using scanning electron microscopy (Helios NanoLab 600, FEI). To evaluate the surface conductivity of the CFS, a 4-point probe technique was applied. Conductivity was calculated using the equation: $\sigma = 1/(R^*w)$, where σ is the electric conductivity, R is surface resistivity (Ω/sq) and w is material thickness (μm). The composition of the scaffolds with and without chemical PPy coatings were investigated with Fourier transform infrared (FTIR) spectroscopy (4000–600 cm^{-1} , Bruker Alpha with Platinum ATR).

3. Results

3.1. Characterization of CFS

3.1.1. FTIR measurements of FS and CFS

To compare the chemical composition of uncoated and coated FS material, FTIR measurements were made and presented in Fig. 1.

Peaks of FS were detected at 3292 cm^{-1} (N–H stretching vibration, specifically inherent to gelatin [27]), 2933 cm^{-1} (CH_2 asymmetric vibration). The 1448 cm^{-1} and 1332 cm^{-1} peaks represent different in plane vibrations [9]. The amide peaks can be identified at 1638 cm^{-1} (amide I), at 1532 cm^{-1} (amide II, mainly NH bending) and at 1242 cm^{-1} (amide III) [27,28]. The 1081 cm^{-1} peak manifests glucose content (mainly CO vibration overlapping with vibration in glucose [29]) [9]. Some peaks for the CFS showed some overlapping with FS such as 3292 cm^{-1} , 1638 cm^{-1} , 1532 cm^{-1} , 1448 cm^{-1} , 1332 cm^{-1} and 1081 cm^{-1} . A strong peak at 1781 cm^{-1} represents C=O group adsorption, due to excess of APS oxidant [5] some PPy particles apparently got overoxidized [30]. The formation of PPy on FS can be seen in typical PPy bands at 1540 cm^{-1} and 1483 cm^{-1} peaks (represent C=C stretching modes [31]). The C=C stretching of aromatic compounds generally occur in the range of 1000–1100 cm^{-1} seen here at 1040 (N–C vibration due to C–H in plane vibrations [5]) and 1071 cm^{-1} (N–C stretching band) [32] with additional peaks at 777 and 708 showing the presence of PPy [33]. The FTIR spectrum shows that the chemically polymerized PPy is indeed deposited on the fiber scaffold, yielding conductive fiber scaffolds (CFS).

3.1.2. SEM images and surface conductivity of FS and CFS

The morphologies of the fiber scaffold and the conductive fiber scaffolds were investigated with SEM, the micrographs are shown in Fig. 2.

The fiber diameter in the FS was 0.8 μm (Fig. 2a and inset), in compliance with recent research [8]. It can be observed that the chemical coating procedure is capable of coating each fiber separately with

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