Electroactive actuator based on polyurethane nanofibers coated with polypyrrole through electrochemical polymerization: a competent method for developing artificial muscles

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Abstract
In the present study, the electrochemical polymerization was carried out to coat the surface of electrospun polyurethane (PU) nanofibers with conductive electroactive polypyrrole (PPy) towards production of Faradaic bending actuators. For this purpose, the surface of electrospun nanofibers was first coated with a thin layer of gold using physical vapor deposition (PVD). PPy was then coated on the surface of prepared nanofibers using different consumed electric charges ranging from 0.5 to 5 C. The produced samples were characterized with respect to surface morphology, electrical properties, electrochemical properties and finally bending actuation performance of the produced actuators. The synthesis of PPy on the surface of nanofibers by the electrochemical polymerization process as well as preservation of the fibrous and porous structure of the samples was confirmed by SEM images. In the polymerization process, the amount of PPy coating on the surface of PU nanofibers increased dramatically with increasing the consumed electric charge. The results of the electrical properties of the produced nanofibrous layers showed that the surface resistivity of the produced PU/PPy nanofibrous layer was decreased from 719.5 to 51.3 Ω/sq for samples produced with the consumed charges of 0.5 and 5.0 C, respectively. Moreover, the electroactive properties of produced actuators were evaluated by cyclic voltammetry technique in a 0.1 M aqueous electrolyte solution of LiClO4 between potentials of −0.6 to 0.8 V. The results revealed that the electroactive properties of produced actuators were improved with increasing the amount of PPy coating. The evaluation of the bending actuation performance of the actuators showed that the angular displacement of the samples produced with consumed charges of 2, 3, 4 and 5 C in a potential cycle was 48°, 153°, 190° and 225°, respectively. These actuators have the potential to be applied in the fields of medicine, robotics and smart textiles.

Keywords: nanofibrous actuator, electrochemical polymerization, polypyrrole, faradaic nature
1. Introduction

Steady progress in smart polymer technology has opened up new horizons for the development of nature-inspired systems due to the potentials of these polymers to detect changes in the environment and respond to external stimuli [1]. In essence, structures made of smart polymers are designed to exhibit certain reactions such as change in shape, size, color, solubility and chain structure when subjected to certain stimuli such as electricity, temperature, pH, solvent, magnetic field, humidity or light [2, 3]. In recent decades, extensive research has been focused on a class of smart polymers known as active polymers, which exhibit mechanical responses, i.e. change in shape and dimension, to environmental stimuli [4]. The electroactive polymer-based actuators developed to suit this specific purpose are known as artificial muscles [5, 6].

Conductive polymers are one of the most important groups of the electroactive polymers, which were first accidentally discovered by Shirakawa et al [7] during their research on polyacetylene. Later, researchers developed several other conductive polymers, of which the most important are polypyrrole (PPy), polyaniline (PANI), polystyrene (PTH), poly(Para-phenylene) (PPP), poly(phenylenevinylene) (PPV) and polyfuran (PF) [8].

In recent years, the actuators manufactured by conducting polymers have attracted great attention by researchers [9–12]. The main mechanism of actuation in these actuators is based on the exchange of ions and solvent molecules between electrolyte solution and polymer structure during the reduction/oxidation electrochemical reactions. In other words, these actuators are electrochemomechanical devices, because during electrochemical reactions, an electric current leads to chemical reactions and changes in composition and volume of the actuator [13, 14]. The small volume changes occurring in conducting polymers during the electrochemical reactions can be converted into linear or bending macroscopic displacements to suit these actuators for various practical applications [15]. These actuators can also be manufactured in various forms, including 2D and 3D films as well as relatively thin fibers [16]. In recent years, the use of fibrous and especially nanofibrous structures of conducting polymers in the production of electroactive actuators has attracted particular attention because of high porosity and high specific surface area provided by fibrous structures, which allow enhanced access to the electrolyte solution [17–19].

Polymeric fibers with a diameter of less than one micrometer also known as polymeric nanofibers, are mainly produced by electrospinning [20, 21]. The electrospinning process involves applying a high voltage to a polymer fluid, i.e. solution or melt, to induce electric charge into the fluid. When the charge reaches a critical level, a jet starts to travel from the tip of the nozzle towards an oppositely charged collector. Along the path, the jet experiences bending instability, which decreases the jet diameter. Also, the solvent can be gradually evaporated and eventually a layer composed of randomly oriented nanofibers is formed on the collector [22, 23].

Production of conducting polymer-based nanofibrous actuators using electrospinning is not easily possible due to the low solubility of these polymers in common solvents as well as their low molecular weight [24]. In this regard, different nanofibrous actuators have been designed by researchers through producing an electrospun nanofibrous substrate with an electrospinnable polymer and then coating the conducting polymers on the surface of nanofibers [25–27]. For example, Zhou et al [28] used polyvinylpyrrolidone/polyvinyl alcohol (PVP) nanofibers produced using a combination of electrospinning and chemical polymerization on the surface of electrospun PVA fibrous actuators, which were coated with PANI through in situ chemical polymerization to produce nanofibrous actuators. They investigated the effect of presence of TiO2 nanoparticles on the mechanical and electrical properties as well as actuation performance of the actuator. In another study by Kwon et al [30], PU nanoﬁbers were coated through PEDOT polymerization in the vapor phase to produce PU/PEDOT bending actuator. In studies recently conducted by our group, PU/PPy bending actuators were produced using a combination of electrospinning processes and in situ chemical polymerization of pyrrole, and their various electrochemical and electrochemomechanical properties were evaluated [32–34].

Although most researchers have focused on the production of actuators using the in situ chemical polymerization of conducting polymers on the surface of electrospun fibers, limited studies reported the electrochemical polymerization method [35, 36]. Therefore, in this study, flexible PU nanofibers were produced by electrospinning and then coated by PPy conducting polymer using electrochemical polymerization. For this purpose, first, the appropriate conditions of electrochemical polymerization on the surface of polymer nanofibers were disclosed and then PU/PPy bending actuators were produced using different consumed electric charges. The surface morphology, electrical and electrochemical properties, bending actuation performance as well as the
Faradaic nature of the produced PU/PPy actuators were also investigated.

2. Materials and methods

2.1. Materials

PU polymer was supplied from DSM Company and used to produce substrate nanofibers. Dimethylformamide (DMF) (>99.8%), pyrrole monomer (>97.0%) and acetonitrile (>99.9%) were purchased from Merck. The pyrrole monomer was distilled under vacuum twice before use. Lithium perchlorate (99.0%) was purchased from Alfa Aesar and used as dopant without any purification.

2.2. Electrospinning PU nanofibers

The production steps of PU/PPy nanofibers are shown schematically in figure 1. Initially, PU nanofibers were produced using a laboratory electrospinning device consisting of a syringe pump, a high voltage power supply and a collector (figure 1(a)). For this purpose, first, a homogeneous PU/DMF solution with concentration of 7 w/v% was prepared. Then, the electrospinning process was performed by adjusting feeding rate, applied voltage and tip to collector distance at values of 0.3 ml h\(^{-1}\), 14 kV and 25 cm, respectively.

Figure 1. Schematic representation of the production steps of PU/PPy nanofibers: (a) producing PU nanofibers by electrospinning, (b) coating of produced nanofibers with a thin layer of gold by using physical vapor deposition (PVD), (c) fixing the nanofibrous layer into plastic frame by double-sided adhesive tape, and (d) the electrochemical polymerization of pyrrole on the surface of PU nanofibers.

Figure 2. The electrochemical cell used during electrochemical experiments of PU/PPy nanofibrous actuator.
2.3. Electrochemical polymerization of pyrrole on the surface of PU nanofibers

It should be noted that in order to use the electrochemical polymerization, it is necessary that the surface of PU nanofibers to be partially electrically conductive. Therefore, prior to the electrochemical polymerization process, the surface of PU nanofibers was coated with a thin layer of gold (figure 1(b)). For this purpose, the pure gold (99.99%) was used and the deposition was conducted by a physical vapor deposition (PVD) system. The pressure of vacuum chamber before evaporation and during coating was $5 \times 10^{-5}$ mbar and $5 \times 10^{-3}$ mbar, respectively. Also, the current and voltage applied to the target were 18 A and 100 V, respectively. The PU nanofibrous layers were fixed on the surface of a holder disk at distance of 30 cm from the target. The coating process was carried out for 20 min on each side of the layers.

To keep the nanofibrous layers smooth and prevent damage during the polymerization process, the specimens were adhered by double-sided adhesive tape inside the plastic frames with a dimension of $10 \times 22$ mm (figure 1(c)). Then, the frames were horizontally embedded in the polymerization solution whose electrical connection was made by small alligator clips. The electrolyte solution of polymerization process was prepared by 0.2 M monomer and 0.1 M LiClO$_4$ as dopant in acetonitrile solvent. Additionally, water with concentration of 2 v/v% was used in the electrolyte solution. It has been confirmed that the use of small amounts of water into organic solvents such as acetonitrile and propylene carbonate results in production of more conductive PPy [37].

Electrochemical polymerization of pyrrole was performed using a SAMA500 potentiostat/galvanostat attached to a personal computer with SAMA500 Version 3.9 software and the gold-coated PU nanofibers were used as the working electrode. In the three-electrode method, the Ag/AgCl (3 M KCl) electrode was used as the reference electrode. In addition, two stainless steel plates (AISI 316) with dimensions of $10 \times 20$ mm were used in parallel as counter electrode, so that the layer of nanofibers was placed between these two plates at a distance of 10 mm (figure 1(d)). The square wave potential method by applying consecutive potentials of $-0.3$ V for 2 s and 0.87 V for 8 s was used at room temperature for electrochemical polymerization of pyrrole on the surface of PU nanofibers. The polymerization process was continued until the desired consumed charge was achieved and thereby PU/PPy nanofibers were produced with different amounts of PPy coating and their properties were evaluated.
The horizontal placement of the nanofibrous layer prevents the potential drop across the layer, resulting in the uniformity of the polymer (PPy) synthesized throughout the layer. It should be noted that before the polymerization process, the solution was purged by nitrogen gas. Additionally, the nitrogen gas flowed above the solution surface during the whole polymerization process.

Figure 6. SEM images of (a) PU, (b) PU/PPy-0.5C, (c) PU/PPy-1C, (d) PU/PPy-2C, (e) PU/PPy-3C, (f) PU/PPy-4C, (g) PU/PPy-5C nanofibers and (h) the cross-sectional of PU/PPy-3C nanofibrous layer.

2.4. Production of nanofibrous bending actuators

For the production of bending actuators and avoiding the curling movements previously observed in nanofibrous conducting polymers-based actuators [35], after coating PU nanofibers using electrochemical polymerization of pyrrole, the produced layers were attached on the nonconducting double-sided adhesive tape. Then, the layers were cut into thin strips of 1 mm wide and 20 mm long and used as an actuator in the electrolyte solution. The mechanical constraint imposed by the passive adhesive layer causes the small
volume changes of the nanofibrous layer to be converted to total bending movement of the actuator.

2.5. Characterization

Scanning electron microscopy (SEM, XL-30, Philips) was used to evaluate the surface morphology of nanofibers produced under different conditions. Simultaneous to SEM imaging, the elements present in the samples were also evaluated using energy-dispersive x-ray spectroscopy (EDX, Seron AIS 2300) at accelerating voltage of 30 kV and detection limit of approximately 0.5 wt%. The average diameter of the nanofibers was also calculated by measuring the diameter of at least 100 randomly selected fibers using Digimizer Version 4.1.1.0 software.

The four-point probe method was used to evaluate the electrical properties of nanofibrous layers coated with different amounts of conducting polymer, and the surface resistance of different samples was measured. The measurements were performed in air at room temperature using four-point probe device (FPN-SN-554, Soraco, Iran). The surface resistance ($R_s$) of samples was calculated using the Van Der Pauw method [38]:

$$R_s = \frac{\pi \frac{V}{I}}{\ln2}$$

where $V$ and $I$ are the voltage and current passing through the specimen, respectively. The term $\frac{V}{I}$ was calculated from the slope of current–voltage characteristic for each sample.

The electrochemical properties of produced actuators were also investigated using SAMA500 potentiostat/galvanostat and its dedicated software (SAMA500, Version 3.9). The nanofibrous actuator and a $1 \times 2$ cm stainless steel plate (AISI 316) were used as the working electrode and the counter electrode, respectively. All potentials are reported relative to the Ag/AgCl (3 M KCl) reference electrode. Also, the aqueous solution of LiClO$_4$ was used as electrolyte. Figure 2 shows this electrochemical cell. The bending actuation of produced actuators was recorded simultaneously with applied potential or electrical current using a video camera and thereby the bending displacement of actuator was calculated at each moment using Digimizer software. As can be seen in figure 2, the angular displacement of produced PU/PPy nanofibrous actuator was obtained by measuring the angle between the surface of electrolyte solution and the actuator tip.

One-way analysis of variance (ANOVA) and Duncan’s multiple range test were used to determine the significance of the results at the significance level of 0.05 using SPSS 21 software.

3. Results and discussion

3.1. Determination of potential window for pyrrole electrochemical polymerization

At the beginning of studies on the electrochemical polymerization of PPy on the surface of PU nanofibers, the preliminary evaluations were conducted to find the potential window of the electrolyte solution as well as the oxidation potential of the pyrrole monomer. The potential window is determined to gain insight into the potential required for pyrrole polymerization, which includes the oxidation of pyrrole monomer, without interfering of the electrolyte reactions. To determine this potential range, the nanofibrous layer was immersed in an electrolyte solution including 0.1 M LiClO$_4$ in acetonitrile solvent containing 2% water between the potentials of $-1.4$ to $1.6$ V at a scan rate of $20$ mV s$^{-1}$ under the test of cyclic voltammetry. Then, the pyrrole monomer with a concentration of $0.2$ M was added to the electrolyte solution and the above experiment was repeated under the same conditions. The results of these surveys are shown in figure 3. As can be seen, no specific electrochemical reaction occurred on the electrode surface in the absence of the pyrrole monomer between the potentials of $-1.2$ to $1.3$ V, and this range could be considered as the potential window of electrolyte (see inset of figure 3). It should be noted that the small reduction current passing during the cathodic scan (about $-0.5$ V) could be due to small impurities in the electrode or electrolyte, which does not influence on detection of proper potential for pyrrole oxidation.

The graphs included in figure 3 also show that the oxidation of pyrrole monomer begins at a potential of about $0.55$ V, indicating the initiation of pyrrole polymerization process at this potential, which leads to darkened surface of PU nanofibrous layer. Therefore, considering the potential window of electrolyte and the initiation potential of monomer oxidation, it can be concluded that the appropriate potential for pyrrole polymerization process in the constant potential method falls in the range of $0.55$ V (the initiation potential of pyrrole oxidation) and $1.3$ V (the initiation potential of electrolyte oxidation). In other words, pyrrole polymerization on the surface of nanofibers in this potential range occurs in the absence of parallel electrolyte reactions. However, overoxidation of PPy can occur at high potentials, which leads to formation of polymer with poor adherence to the electrode.
surface as well as decrease in conductivity and electroactivity of synthesized polymer. Therefore, potentials of less than 1.0 V are usually used for polymerization of PPy to prevent its overoxidation [39, 40]. In addition, the results show that galvanostatic (constant current) electrochemical polymerization could be done using electric currents up to 2 mA without any electrolyte oxidation reactions.

It should be noted that it is necessary to renew the electrolyte solution for each polymerization process and use a fresh solution for subsequent polymerization, because reuse of the electrolyte solution leads to weakened electrical properties of the synthesized PPy. The results showed that using the electrolyte solution for the third time decreases the electrical conductivity of produced PU/PPy nanofibrous layer by about 55%. This phenomenon is probably due to the presence of by-products produced during previous polymerization processes [37].

Figure 8. EDX results of PU nanofibers (a) before and (b)–(f) after coating with PPy by total consumed charges of (b) 1 C, (c) 2 C, (d) 3 C, (e) 4 C, and (f) 5 C in the electrochemical polymerization process.

Table 1. Surface resistivity of PU/PPy nanofibrous layer produced using different amounts of total consumed charges during the electrochemical polymerization process.

| Sample  | Total consumed charge (C) | Surface resistivity (Ω/sq) |
|---------|--------------------------|---------------------------|
| PU      | —                        | 185.9 ± 4.1               |
| PU/PPy-0.5 C | 0.5                 | 719.5 ± 29.2             |
| PU/PPy-1C  | 1.0                     | 184.5 ± 11.6              |
| PU/PPy-2C  | 2.0                     | 134.2 ± 4.8               |
| PU/PPy-3C  | 3.0                     | 70.6 ± 3.4                |
| PU/PPy-4C  | 4.0                     | 60.8 ± 2.8                |
| PU/PPy-5C  | 5.0                     | 51.3 ± 1.7                |
In the electrochemical polymerization process, the amount of electric charge consumed in the process [37, 41]. Therefore, using this factor, different PPy coatings on the surface of PU nanofibers were created and the final properties of the produced PU/PPy nanofibers were evaluated. Using the square wave potential method results in desirable morphology, higher electrical conductivity as well as greater flexibility of the synthesized polymer [42, 43]. Pyrrole polymerization was performed by applying consecutive potentials of $-0.3 \text{ V}$ for 2 s and 0.87 V for 8 s. Under these conditions and at times of anodic potential of 0.87 V, PPy was gradually coated on the surface of PU nanofibers. Therefore, the color of nanofibers was gradually darkened and changed to black. At the end of the polymerization process, nanofibrous layer was partially oxidized using voltage of 0.87 V for 60 s at room temperature to prevent oxygen attack, which reduces the capacity of its redox processes. This process also leads to partially increase in the consumed charge of polymerization (for example, about 0.1 C in PU/PPy-3C sample), which is small compared to the total consumed charge during electrochemical polymerization of pyrrole on the surface of PU nanofibers. It can be tracked the electric current and the consumed charge in the electrochemical polymerization process, simultaneously with the application of potential steps. For example, the chronocoulometric response, i.e. consumed charge versus time, during the polymerization process to achieve the total charge of 3 C is shown in figure 4.

As can be seen in figure 4, the charge of 3 C is consumed in the polymerization process during the time of about 3400 s. PU nanofibrous layer before and after the electrochemical polymerization process is shown in figure 5. As evident, the color of PU nanofibrous layer changes from golden to black after the polymerization process, indicating coating the conducting PPy on the surface PU nanofibers.

In order to synthesize different amounts of PPy on the surface of PU nanofibers, the square wave potential method was used and the total charges of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 C were consumed in polymerization process. The resultant nanofibers were named as PU/PPy-0.5 C, PU/PPy-1C, PU/PPy-2C, PU/PPy-3C, PU/PPy-4C and PU/PPy-5C, respectively. After producing PU and PU/PPy nanofibers using different consumed charges, their surface morphology was evaluated using SEM images shown in figures 6(a)–(g). Also, a typical cross-sectional SEM image of PU/PPy nanofibrous layer is shown in figure 6(h). The SEM results indicated that the PU nanofibers (after coating with gold) have a uniform morphology and no bead defects were present. Also, the amount of coated PPy on the surface of PU nanofibers increases significantly by increasing the electrical charge consumed during the polymerization process. In addition, it is observed that the porous and fibrous structure of nanofibrous layers has been completely preserved, irrespective of total consumed charge. PU/PPy nanofibers have a rougher surface morphology compared to PU nanofibers and PPy coating grows as granular or spherical nanostructures on the surface of the nanofibers during the electrochemical polymerization process.

The results indicated that the diameter of PU/PPy nanofibers significantly increased with increasing total consumed charge during polymerization process. The diameter of nanofibers versus consumed charge is depicted in figure 7. As can be seen, the diameter of the produced PU/PPy nanofibers increased from 306 to 455 nm using the total consumed charge of 0.5 C for pyrrole polymerization, and reached 1049 nm in the sample with the total consumed charge of 5.0 C. Obviously, this is due to increasing the amount of PPy coating on the surface of PU nanofibers with increasing the consumed charge. It is worthy to note that significant effect of the total consumed charge during the electrochemical polymerization on the diameter of produced nanofibers was verified by one-way ANOVA. In addition, the Duncan test results showed that there was a significant difference in the diameter of produced nanofibers between all samples.

EDX analysis of PU nanofibers before and after coating with PPy using different total consumed charges in the electrochemical polymerization process is shown in figure 8. As evidenced by figure 8, only the peaks related to C and O elements are present in the spectrum of PU nanofibers. In contrast, N and Cl elements are observed in the spectrum of PPy-coated samples in addition to C and O elements, indicating the presence of PPy conducting polymer on the surface of PU nanofibers. The presence of Cl element in PU/PPy nanofibers indicates the doping of PPy with ClO$_4$ ions. As the consumed charge increases, the amount of doped PPy on the surface of the nanofibers increases. The increase of Cl element with increasing the total consumed charge indicated an increase in the amount of doped PPy on the surface of PU/PPy nanofibers. Also, the peaks at 2.12 keV (big peak) and 9.71 keV in the spectrum of all samples before and after PPy
electropolymerization, are attributed to gold (Au) coated on the surface of samples before SEM imaging and PVD process.

Dependency of electrical properties of PU/PPy nanofibrous layer on total consumed charge during the electrochemical polymerization process and consequently the amount of coated PPy was also investigated. For this purpose, the surface resistivity of produced samples was measured by the four-point probe method. The surface resistivity of PU/PPy nanofibrous layers produced using different amounts of total consumed charge during the polymerization process is presented in Table 1.

As can be seen, after coating with gold, the surface resistivity of PU nanofibrous layer was obtained as $185.9 \pm 4.1 \ \Omega/\text{sq}$, which is sufficient for synthesis of PPy on the surface of PU nanofibrous layers using the electrochemical polymerization method. Also, the results showed that the surface resistivity of samples decreases significantly with increasing the conducting polymer coating. Such that the surface resistivity of produced PU/PPy nanofibrous layer decreased from 719.5 $\Omega/\text{sq}$ for the PU/PPy-0.5 C sample to 51.3 $\Omega/\text{sq}$ for the PU/PPy-5C sample. PU/PPy-0.5 C sample with consumed electric charge of 0.5 C during the polymerization process has a relatively high surface resistivity, which is much higher than that of gold-coated PU nanofibers. This indicates that the synthesized PPy coating on the surface of nanofibers is insufficient. The surface resistivity decreases dramatically by increasing the total consumed electric charge to 1.0 C. The decrease in surface resistivity of nanofibrous layers by increasing the consumed charge during the electrochemical polymerization process is due to the increased coating thickness of PPy conducting polymer. In other words, increasing the coating amount of PPy on the surface of PU nanofibers yields to improved electrical connection at the intersection points of nanofibers, which reduces the total electrical resistance of the layer.

### 3.3. Electrochemomechanical performance of PU/PPy nanofibrous actuators

The electroactive properties and actuation performance of manufactured actuators were investigated after coating PU nanofibrous layers with PPy conducting polymer. The presence reversible electrochemical oxidation and reduction processes is indicating of electroactivity of a sample [44]. The cyclic voltammetry responses for PU/PPy nanofibrous actuators produced using the total consumed charges of 2.0–5.0 C in the 0.1 M LiClO$_4$ electrolyte solution in potentials ranging between $-0.6$ and $0.8$ V with scan rate of 5 mV s$^{-1}$ are shown in Figure 9. All reported voltammetric responses are related to the third potential cycle after reaching a stationary voltammetric response. The samples produced with total consumed charges of 0.5 and 1.0 C were not electroactive enough to exhibit stable and reversible electrochemical reactions and therefore suitable graphs were not achieved. As can be seen, PU/PPy nanofibrous layers produced using the total consumed charges of 2.0–5.0 C display electroactivity. Additionally, with increasing the total consumed charge in the polymerization process, which yields to the thicker coating of PPy on the surface of PU nanofibers, the
electroactivity was further enhanced. As the total consumed charge changes, the potential as well as current of anodic and cathodic peaks of samples also changes. The potential difference between the cathodic and anodic peaks was decreased as the consumed charge increased from 2.0 to 5.0 C. For example, the oxidation and reduction peaks are observed at the potentials of 0.70 and $-0.1\,\text{V}$ for the sample produced using total consumed charge of 3.0 C. These peaks appear at the potentials of 0.35 and $-0.28\,\text{V}$ when total consumed charge becomes 5.0 C. This decreased difference is due to the increase in PPy coating and consequently the increased electrical conductivity of the nanofibers. The larger difference between the redox peaks is due to lower conductivity of sample which causes a larger potential drop [18].

During the oxidation process of produced actuators, the electrons are extracted from PPy structure and in the reduction process electrons are injected into it. Therefore, the perchlorate anions and water molecules enter the polymer structure from the electrolyte solution during the oxidation process of the actuators. They leave the polymer structure during the reduction process to balancing the electric charge and osmotic pressure. As shown in schematic representation of figure 10, this phenomenon results in a change in the volume and therefore in the bending angle of produced actuator due to the mechanical constraint imposed by the inactive adhesive tape.

The change in actuator angle with the application of potential was also measured simultaneously to investigate the effect of total consumed electric charge during the polymerization process on the bending actuation performance of PU/PPy nanofibrous activator. The dynamo-voltammetric responses, i.e. angle versus potential, of these actuators in potential range of $-0.6$ to $0.8\,\text{V}$ with a scan rate of $5\,\text{mV\,s}^{-1}$ in the 0.1 M LiClO$_4$ electrolyte solution are displayed in figure 11.

As can be seen, regardless of total consumed charge, the entrance of the perchlorate anions from the electrolyte solution into the actuator structure during the oxidation reaction is accompanied by increasing the volume of actuator and thus its anticlockwise angular displacement. In the reduction process, the egress of anions leads to decrease in the volume and consequently the clockwise displacement of actuator. The position of the different produced actuators in reduced and oxidized states is shown in figure 12.

By increasing the total electric charge consumed during pyrrole polymerization process, which results in an increase in the thickness of PPy coating on the surface of PU nanofibers, the amount of bending actuation of produced actuators...
also increased significantly. The total bending actuation in each sample is obtained by measuring the anticlockwise displacement of the actuator during the oxidation process. The results of this evaluation show that total bending actuation of the nanofibrous actuators produced using total consumed charges of 2.0, 3.0, 4.0 and 5.0 C is 48°, 153°, 190° and 225°, respectively. As expected, actuators with more electroactivity exhibit higher bending actuation. Also, the obtained angular displacement using these nanofibrous actuators are significantly higher compared to the some actuators made of conductive polymer films [45–47]. Therefore, according to the results, superior actuation performance is observed for PU/PPy nanofibrous layers produced by electrochemical polymerization method especially using total consumed electric charges of 3 C and more.

3.4. Faradaic nature of PU/PPy nanofibrous actuators produced by electrochemical polymerization

The bending actuators based on the conductive polymer films are well-known as Faradaic motors, so that the angular displacement and speed of the actuator are controlled by the consumed electric charge in the actuation process and the applied electric current to the actuator, respectively [45, 46, 48]. Also, the results of our previous research revealed that the nanofibrous actuators produced by chemical polymerization have Faradaic nature [33]. In this section, the Faradaic behavior of PU/PPy nanofibrous actuators produced by electrochemical polymerization is explored. The related results are shown in figure 13. Initially, after a few voltammetric cycles, PU/PPy nanofibrous actuator (PU/PPy-3C

![Figure 12](image-url) Position of PU/PPy nanofibrous actuators produced using total consumed charges of (a) 2 C, (b) 3 C, (c) 4 C and (d) 5 C in reduced and oxidized states.
was electrochemically stimulated in 1 M LiClO₄ aqueous electrolyte solution using various constant currents. For each test, the applied current continued until the actuator reached a 90° angle. The obtained chronopotentiometry responses after applying currents of 0.2–0.8 mA are presented in figure 13(a). As can be seen, the time required to reach 90° angular displacement of actuator is reduced by increasing the applied electric current. The angular velocity of produced nanofibrous actuator was calculated by measuring the time required for actuator to reach an angular displacement of 90°. The angular velocity of actuator in terms of applied electric current is shown in figure 13(b) according which the angular velocity of the nanofibrous actuator produced by the electrochemical method is much greater than that produced by the chemical polymerization method. This can be interpreted by a higher rate of ion diffusion in the oxidation process of actuator produced by electrochemical polymerization. Therefore, it can be said that using electrochemical polymerization as a competent method for the production of PU/PPy nanofibers yields to a significant improvement of the performance of manufactured actuator. It should be noted that according to the literature [49], the conductive polymers-based film actuators produced using the electrochemical polymerization show better performance over those produced by the chemical polymerization method.

Also, the amount of electric charge consumed in the actuation process of produced actuators can be obtained by considering the time of angular displacement of actuator in each applied electric current. The consumed electric charge in the actuation process of PU/PPy nanofibrous actuator versus applied current is shown in figure 13(c). As can be seen, the consumed electric charge is approximately a constant value of 13 mC for a 90° angular displacement of actuator regardless of applied electric current. These results indicate that the angular displacement of PU/PPy nanofibrous actuator...
produced by electrochemical method is controlled by the consumed electric charge in its actuation process and the equation of $\alpha = K \frac{Q}{I}$ is established. According to this equation, the same consumed electric charge results in the same angular displacement of actuator. Moreover, the consumed electric charge of the actuator to reach different angles from 15° to 180° was calculated in applied electric currents of 0.2–0.8 mA. The results are displayed in figure 13(d) according which the consumed electric charge of the actuator is constant at different angles for all applied electric currents. The slope of this plot, which shows the amount of electric charge needed for 1° angular displacement of the actuator, was obtained as 0.097 mC deg⁻¹. Using this characteristic, the electric charge required for any desired actuator angular displacement could be calculated. The obtained results demonstrate the Faradaic nature of PU/PPy nanofibrous actuator produced by electrochemical polymerization. Large and controlled displacements of these actuators make them suitable candidates for various advanced applications such as artificial muscles.

4. Conclusion

In this research work, the nanofibrous bending actuators were developed based on conducting polymer of PPy using a combination of electrospinning and electrochemical polymerization. The square-wave potential technique was used in the electrochemical polymerization process, and different amounts of conducting polymer were synthesized on the surface of electrospun PU nanofibers by controlling the consumed electric charge. According to the results of this study, actuators produced using total consumed electric charges of 2–5 C are electroactive. During the actuation in LiClO₄ electrolyte solution, the electrochemical oxidation and reduction reactions lead to transfer of perchlorate anions as well as water molecules within the structure of actuators, which results in angular displacement. The results revealed that the total angular displacement of the produced actuators increased significantly with increasing the coating amount of PPy conducting polymer on the surface of PU nanofibers. In this regard, the angular displacement in a potential cycle was 48° and 225° for PU/PPy-2C and PU/PPy-5C actuators, respectively. The produced actuators exhibited a Faradaic nature so that their angular velocity was linearly correlated with the applied electric current. Additionally, it was demonstrated that the angular displacement of produced actuators is a function of the electric charge consumed during the actuation process. Overall, the electrochemical polymerization is an efficient method for coating the electrosprun nanofibers with conducting polymers to produce nanofibrous actuators.

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