Fabrication of Conductive Fabric as Textile Electrode for ECG Monitoring

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Abstract: To develop textile electrodes for electrocardiogram (ECG) monitoring, cotton woven fabric was coated with polypyrrole via electrochemical polymerization process. A two-step polymerization process was conducted, i.e. via chemical polymerization to make cotton fabric electric conductive and then electrochemical polymerization. Evaluations of the electrodes in terms of electrical resistance and electrochemical impedance spectroscopy were made to examine the progress of electric performances after each processing step. The results show that, after electrochemical polymerization process, the conductivity of the electrode is increased and the quality in transferring electrical signals improved.

Keywords: Textile electrode, Polypyrrole, Cotton fabric, Electrocardiogram, Electrochemical polymerization, Electrochemical impedance spectroscopy

Introduction

In real-time monitoring of electrocardiogram (ECG) signals, textile electrodes characterized by wear comfort can provide good user experience to patients in monitoring ECG signals [1]. Conductive fabrics, the main element of textile electrodes, can be made through different processes, such as co-weaving with yarns of metal or mental coating [2-5], fabric coating with conductive polymers [6-11], and etc. Among them, coating with polymers has been proven an effective method [12] and an example of monitoring ECG signals through *in-situ* polymerized polypyrrole-coated Lycra fabrics has been demonstrated [6].

Polypyrrole (PPy) is a well known conductive polymer with many excellent characteristics [13], which make PPy an ideal choice as a coating polymer for textile electrodes. Coating PPy on fabrics can be made via *in-situ* chemical polymerization or electrochemical polymerization. It is known that electrochemical polymerization is a more controllable polymerization process resulting in better coating quality [13-15]. Also, the process can deposit a thicker polymer film than chemical polymerization on the substrate with less defects [16,17] and make the coating more electric conductive. However, to the best of authors' knowledge, ECG monitoring electrodes made from fabrics coated via electrochemical polymerization has not been reported, although conductive fabrics has been developed for magnet shielding and other novel applications [16].

In this study we report a two-step processing method for fabricating textile electrodes made from cotton fabric coated with polypyrrole via first *in-situ* chemical polymerization and then electrochemical polymerization. A cotton woven fabric of plain weave was chosen as the substrate and PPy as coating polymer. After the coating process the samples were observed by scanning electron microscope (SEM) and characterized by electric resistance, electrochemical impedance spectroscopy (EIS) and ECG signal monitoring. We hope that the experiments would throw some light on understanding the performances of the textile electrode fabricated by the process in ECG monitoring.

Experimental

Materials

Pyrrole (Py, Sinopharm Chemical Reagent Co., Ltd.) was stored dark in a sealed container at 0 °C before use. Ammonium peroxydisulfate (APS, Sinopharm Chemical Reagent Co., Ltd.) and sodium dodecyl benzene sulfonate (SDBS, Sinopharm Chemical Reagent Co., Ltd.) were used as oxidant and dopant, respectively, in chemical polymerization. Anthraquinone-2-sulfonic acid sodium salt (AQSA-Na, Sinopharm Chemical Reagent Co., Ltd.) was used as a supporting electrolyte in electrochemical polymerization. The weight of the plain woven fabric was 112 g/m² and the warp and weft density was 52 ends/cm and 28 ends/cm, respectively.

Fabrication Process

Samples of cotton fabric coated with PPy (hereinafter named PPy/cotton) was fabricated by a two-step process, i.e. first via *in-situ* chemical polymerization to make it conductive and then electrochemical polymerization. Before the process, the fabric was cut into a square of 3.5×3.5 cm, washed in an aqueous solution including scouring agent and sodium hydroxide for 1 h to remove possible grease and other impurities.

In the solutions for chemical polymerization, the concentrations of pyrrole, APS (oxidant) and SDBS (dopant) were 0.04 M, 0.02 M and 0.009 M, respectively, to ensure a good conductivity [13]. The fabric samples were immersed in the

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	Cotton fabric	CP sample	CCP sample	ECP sample
Weight (g)	0.1374±0.0013	0.1580 ± 0.0038	0.1701 ± 0.0010	0.2170±0.0029
Weight gained (%)	-	14.99	23.80	57.93

Note: The sample number within each group is four. F-test shows that, at 0.01 significant level, there is significant difference between the samples from different groups.

solution of APS and SDBS and kept at 0 °C for 30 min, followed by adding into the solution a uniformly dispersed pyrrole solution to initiate chemical polymerization. The process was kept at 0 °C for 2 h. The samples were then rinsed thoroughly with distilled water and dried in an oven at 80 °C for 20 min. The samples via chemical polymerization are hereinafter labeled CP samples.

Electrochemical polymerization was processed under a constant current density of 1 mA/cm² by using an electrochemical workstation (600D, CH Instruments, Inc.). In the process, a CP sample and a stainless steel net were used as the working and counter electrodes, respectively. The concentration of AQSA-Na in the supporting electrolyte was 0.3 M and that of pyrrole was 0.3 M. After the process at 0 °C for 2 h, the samples were rinsed thoroughly with distilled water and then dried in an oven at 80 °C for 20 min. The samples via electrochemical polymerization are hereinafter labeled ECP samples.

For comparison, controlled samples were fabricated in a parallel process to the electrochemical polymerization, i.e. CP samples were processed through chemical polymerization once more following the same procedures aforementioned. The samples via twice chemical polymerization are named CCP samples.

All the samples were weighed by an electronic scale (BSA 224S-CW, Sartourius) and the results are listed in Table 1. It shows that, by comparison to CP samples, both CCP and ECP ones gain more weights indicating thicker PPy coating films. Among those, samples via electrochemical polymerization gain more weights than their counterparts via twice chemical polymerization.

Results and Discussion

Electric Resistance

Figure 1 shows the setup to measure the electric resistance of samples in their thickness direction. During the measurement, a PPy/cotton sample was placed between the two copper plates, on which a constant pressure of 3.55 kPa was applied to ensure a good contact. The reason for the chosen pressure was that it was within the range of comfort wearing [18], and that the testing results were less sensitive to the variation of the pressure within the range for ECG measurement. The ambient atmospheric condition was (20 ± 2) °C and (65 ± 3) % RH.

It is seen from Table 2 that, after the first step of



Figure 1. Electric resistance measurement.

Table 2. Electric resistance of samples after polymerization

Electric resistance (Ω) 1,296.9	92±68.74 74	41.40±2.78	324.62±10.06

Note: The number of the samples within each group is four. F-test shows that, at 0.01 significant level, there is significant difference between the samples from different groups.



Figure 2. SEM of PPy/cotton samples; (a) cotton fabric before polymerization, (b) CP sample, via chemical polymerization, (c) CCP sample, via twice chemical polymerization, and (d) ECP sample, via first chemical and then electrochemical polymerization.

fabrication by chemical polymerization, the fabric became electric conductive because of PPy coating. Then, as expected from Table 1, the electric resistance reduced dramatically for the samples after the second step of process by electrochemical polymerization. It can also be expected that the samples via twice chemical polymerization (CCP samples) increased their conductivity due to more PPy coating, but to a less extent by comparing to their counterparts via electrochemical polymerization.

The surface morphology of PPy/cotton samples can be observed from their SEM images (Quanta 250) in Figure 2, in which a noticeable change on the surface of the samples in respect to PPy coating were clearly illustrated. The surface of the cotton fibers is rather smooth, showing an intense roughness with small wrinkles, as in Figure 2(a). Chemical polymerization of PPy leads to the formation of conductive, dense and homogeneous nano coatings on the fabric surface as in Figure 2(b). Further step of process, by either chemical or electrochemical polymerization, results in more clusters and/or nodular nanoparticles on the fiber surface with some aggregation of spherical nanoparticles on the fiber surface, as in Figures 2(c) and 2(d). With electrochemical polymerization, there are more PPy conductive nanoparticles on the coating film comparing with its counterparts with chemical polymerization.

Electrochemical Impedance Spectroscopy

During ECG signal monitoring, an electrochemical reaction takes place in the interface between human skin and electrodes. This is a phenomenon that converts ionic current into electronic current and can be characterized by sample's electrochemical impedance spectroscopy (EIS), a technique that probes energy storage and dissipation properties over a range of frequencies.

The impedance of the samples was measured by the electrochemical workstation used in the process of electrochemical polymerization. The electrolyte consisted of 20 g/l NaCl and 1 g/l urea with a pH of 5.8, typical values as human sweat [4]. Figure 3 shows typical Nyquist plots of



Figure 3. Nyquist plots of PPy/cotton electrodes, insert showing details in high frequency region.

PPy/cotton samples from the three polymerization processes. All of them show the typical electrochemical behaviors of polypyrrole [19]. By a comparison of the semicircles in the high frequency region towards the origin in Figure 3, according to Wang *et al.* [20], it is clear that the two-step polymerization process, both chemical-chemical and chemical-electrochemical, reduces significantly the charge-transfer resistance of PPy/cotton samples at the interface between the PPy coating and electrolyte, indicating a great improvement in electric conductivity. Further comparison, referring to the insert in Figure 3, indicates that the electric conductivity of PPy coating via electrochemical polymerization offers much smaller resistance converting ionic current into electronic current than that via the process of twice chemical polymerization.

The curves in Figure 3 can be modeled by an interfacial equivalent circuit in Figure 4. In the circuit R_s is the resistance of the electrolyte between the working electrode and reference electrode in the electrochemical workstation and it remains constant during the experiment for all the samples. R_{ct} represents the transfer resistance from ionic charge of the electrolyte to electron charge of the electrode and it is the key parameter in the performance evaluation of PPy/cotton samples. Constant phase element (CPE) is an equivalent capacitor with two parameters, CPE-T and CPE-P. The former represents the capacitance of the interface while the latter is a constant between 0 and 1. When CPE-P=1, CPE could be treated as an ideal capacitor, while when CPE-P=0, CPE is a pure resistor.

The parameters of the circuit are calculated by fitting the curves in the high frequency range of Nyquist plots with the equivalent circuit and listed in Table 3.

It is seen from Table 3 that, for all the samples, CPE shows predominantly the nature of pure capacitance because the values of CPE-P are all closing to 1.0. Then, the greatest value of CPE-T of ECP sample implies the greatest capacitance of the sample due possibly to the larger contact area between the electrode and electrolyte because of more



Figure 4. Equivalent circuit modeling polypyrrole/electrolyte interface.

Table 3. Parameters of the equivalent circuit

	CP sample	CCP sample	ECP sample
$R_{s}(\Omega)$	4.96	4.57	4.78
CPE-T (F)	7.28×10 ⁻⁵	1.37×10 ⁻⁴	3.80×10 ⁻⁴
CPE-P	0.82	0.88	0.77
$R_{ct}(\Omega)$	75.29	21.26	5.47



Position of the electrode

Figure 5. Schematic diagram of ECG signal recording.



Figure 6. ECG signals monitored by (a) Ag/AgCl electrodes, (b) CP electrodes, (c) CCP electrodes, and (d) ECP electrodes.

PPy nanoparticles formed during polymerization process. Further, values of R_{ct} show a great reduction in the chargetransfer resistance of ions of ECP sample indicating a more favorite condition provided by electrochemical polymerization for electric signal transformation than chemical one.

ECG Monitoring

PPy/cotton samples were cut into the size of conventional Ag/AgCl electrodes of circular shape with a diameter of 3.0 cm, and then replaced the latter in ECG measurements with an amplifier (AD620, Analog Devices Inc) and a digital oscilloscope (TDS 3052B, Tektronix). The schematic diagram of ECG signal recording is shown in Figure 5. Following the lead I of the standard bipolar limb leads [21], three electrodes were attached on the outer skin of a healthy male volunteer without any heart disease histories, two on each forearms and one on his right leg.

The textile electrodes were conditioned at (20 ± 2) °C and (65 ± 3) % RH for 24 h before use. Before ECG measurement the volunteer was sitting quiet for 0.5 h. Then, the skin was cleaned with medical alcohol. After the attachment of the electrodes at the positions illustrated in Figure 5, ECG signals were recorded. Typical ECG signals are given in Figure 6, in which the signals by conventional Ag/AgCl electrodes are also displayed as a reference. From the recorded signals we can identity the typical ECG of QRS-complex, P-wave and T-wave.

The results are in accord with the analyses in the section of Electrochemical Impedance Spectroscopy, i.e. the quality of the ECG signals by ECP electrodes has a much better quality with less noise than CP and even CCP ones. From the insert spectrum graphs it would be interesting to notice that the power line interference at 50 Hz is the dominate frequency of noise. The low noise by ECP electrodes could, therefore, be attributed to the improvement of static electric property and ion exchange performance when fabric is coated by electrochemical polymerization. The results can also be expected because the low impedance for ECG signals would increase the effective common mode rejection ratio of the instrumentation amplifier [22], resulting in noise attenuation.

Conclusion

In this study we reported a two-step polymerization process to fabricate PPy/cotton textile electrodes for ECG signals monitoring. The process includes first the process of chemical polymerization to make cotton fabric electric conductive and then electrochemical polymerization. Electric resistance in the thick direction of PPy/cotton sample is reduced dramatically from about 1297 Ω of chemical polymerized sample to 325 Ω of electrochemical polymerized one under a pressure of 3.55 kPa, showing a great improvement in electrical conductivity. Nyquist plots and the equivalent circuit indicate that there is an obvious reduction in chargetransfer resistance in favor of the electrochemical polymerized samples. The reduction in the impedance of textile electrodes in ECG signal transfer will also bring the beneficial effects of attenuating dominating noise induced by the power line interference at 50 Hz and improves the recording quality of ECG signals. The performances of PPy/cotton electrodes demonstrate the feasibility and reliability of the two-step polymerization process in fabricating textile electrodes for ECG signals monitoring.

References

- L. Beckmann, C. Neuhaus, G. Medrano, N. Jungbecker, M. Walter, T. Gries, and S. Leonhardt, *Physiol. Meas.*, **31**, 233 (2010).
- L. Li, S. Liu, F. Ding, T. Hua, W. M. Au, and K.-S. Wong, *Text. Res. J.*, 82, 2062 (2012).
- V. Marozas, A. Petrenas, S. Daukantas, and A. Lukosevicius, J. Electrocardiol., 44, 189 (2011).
- G. Priniotakis, P. Westbroek, L. Van Langenhove, and C. Hertleer, *Trans. Inst. Meas. Control*, 29, 271 (2007).
- P. Westbroek, G. Priniotakis, E. Palovuori, K. De Clerck, L. Van Langenhove, and P. Kiekens, *Text. Res. J.*, 76, 152 (2006).
- D. D. Ross, F. Carpi, F. Lorussi, A. Mazzoldi, R. Paradiso, E. P. Scilingo, and A. Tognetti, *Autex Res. J.*, 3, 180 (2003).
- S. Tsukada, H. Nakashima, and K. Torimitsu, *PLoS ONE*, 7, 33689 (2012).
- 8. B. Yue, C. Wang, X. Ding, and G. G. Wallace, Electrochim.

Acta, 68, 18 (2012).

- B. Yue, C. Wang, P. Wagner, Y. Yang, X. Ding, D. L. Officer, and G. G. Wallace, *Synth. Met.*, **162**, 2216 (2012).
- L. Zhu, L. Wu, Y. Sun, M. Li, J. Xu, Z. Bai, G. Liang, L. Liu, D. Fang, and W. Xu, *RSC Adv.*, 4, 6261 (2014).
- 11. G. Liang, L. Zhu, J. Xu, D. Fang, Z. Bai, and W. Xu, *Electrochim. Acta*, **103**, 9 (2013).
- 12. S. A. Odhiambo, C. Hertleer, A. Schwarz, and L. Van Langenhove, *Text. Res. J.*, 84, 347 (2014).
- M. S. Kim, H. K. Kim, S. W. Byun, S. H. Jeong, Y. K. Hong, J. S. Joo, K. T. Song, J. K. Kim, C. J. Lee, and J. Y. Lee, *Synth. Met.*, **126**, 233 (2002).
- L. Hu, J. Tu, S. Jiao, J. Hou, H. Zhu, and D. J. Fray, *Phys. Chem. Chem. Phys.*, 14, 15652 (2012).
- Y. Yao, N. Liu, M. T. McDowell, M. Pasta, and Y. Cui, Energ. Environ. Sci., 5, 7927 (2012).
- K. F. Babu, R. Senthilkumar, M. Noel, and M. A. Kulandainathan, *Synth. Met.*, **159**, 1353 (2009).
- J. Molina, A. I. del Río, J. Bonastre, and F. Cases, *Eur. Polym. J.*, 44, 2087 (2008).
- H. Morooka, R. Fukuda, M. Nakahashi, H. Morooka, and H. Sasaki, *Sen-I Gakkaishi*, 61, 55 (2005).
- X. Ren and P. G. Pickup, J. Electroanal. Chem., 420, 251 (1997).
- K. Wang, J. Huang, and Z. Wei, J. Phys. Chem. C, 114, 8062 (2010).
- P. J. Xu, H. Zhang, and X. M. Tao, *Text. Prog.*, 40, 183 (2008).
- L. Rattfalt, F. Bjorefors, D. Nilsson, X. Wang, P. Norberg, and P. Ask, *Biomed. Eng. Online*, 12, 64 (2013).