Electrochemical thin film deposition of polypyrrole on different substrates

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Abstract

Polypyrrole is one of the important conductive polymers that are widely used in energy storage systems, biosensors and electronics. The electrochemical synthesis of polypyrrole has advantages of simple process, mass production and low cost. In this study, polypyrrole thin films were deposited on different electrode substrates by cyclovoltammetric (CV), galvanostatic and potentiostatic deposition methods. Results demonstrated that the galvanostatic deposition method could provide higher electrochemical activity for the films. Different electrode materials including gold, glassy carbon and ink-made carbon composite electrodes were investigated for polypyrrole deposition. The conductive films on all substrates exhibited p-type conjugate polymer characteristics. However, the substrate properties had great impact on the stability of the deposited thin film and some composite carbon substrate materials demonstrate the best performance. The mechanism of the instability of polypyrrole was suggested. The study also demonstrates the feasibility of using carbon ink to make composite electrodes for possible applications in energy storage systems and electrochemical sensors.

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1. Introduction

Since polypyrrole was first electrochemically synthesized more than two decades ago by Diaz et al. [1], it has been intensively investigated. Polypyrrole is an intrinsically conducting polymer, and its thin and plastic film has many possible applications [2] such as capacitors [3], electrochromic devices [4], anti-corrosive coatings [4], batteries [5], actuators [6] and sensors [7]. The advantages of electrochemical deposition of polypyrrole are that films can be prepared simply with one-step procedure and exact control of thickness. There have been many works dealing with preparation of thin polypyrrole films [8] and influence of the preparation conditions on the properties of electrochemically polymerized polypyrrole. The preparation conditions studied include deposition current, deposition potential, and composition of deposition solutions. However, there are needs to further investigate effects of different substrate electrode materials on properties of polypyrrole films. Moreover, some important applications of polypyrrole such as batteries, chemical and biological sensors are used in aqueous solutions experienced instability problems [9,10], and also require development of robust polypyrrole films stable in aqueous solution.

In this study, we investigated electrochemical deposition of polypyrrole with different substrate electrode materials. The screen-printing microfabrication technology has advantages of flexibility, low cost, high reproducibility and high-throughput mass production, and thus is widely used in electronic components, energy storage systems and electrochemical sensors. Carbon inks are preferred materials for screen-printed electrodes due to their extremely low cost. Screen-printed carbon electrodes were evaluated for polypyrrole deposition in this report. We particularly addressed the problem of polymer instability in aqueous solutions and identified the influence of substrate materials on polypyrrole stability.

2. Experimental

EG&G PAR-273A potentiostat was used to conduct cyclovoltammetry and electrolysis experiments for polypyrrole deposition. Solartron 1260+1287 were used for
impedance and cyclic voltammetry measurements. Glassy carbon electrode (3-mm diameter, CHI), gold electrode (3 mm, CHI) and homemade carbon composite electrodes, fabrication method is described later, were used as working electrodes. The working, reference (Ag/AgCl) and auxiliary electrodes (Pt sheet) were placed in 10 ml beaker cell for electrochemical experiments.

All chemicals including phosphate buffered saline (PBS) (Sigma-Aldrich), pyrrole (Sigma-Aldrich), carbon inks DuPont 7102, 7105 (DuPont Electronic Materials), TU 158 (Asahi) and insulation ink (Ercon R-486 (AH) Blue) were used as received.

Carbon composite working electrodes were screen-printed from carbon inks through a patterned (100-µm

Fig. 1. Cyclic voltammograms of polypyrrole films deposited with different methods: (1) electrolysis at constant current; (2) CV; (3) electrolysis with constant potential; solution: 0.1 M PBS.

Fig. 2. Impedance measurements at galvanostatically deposited polypyrrole film on DuPont 7012 electrode with different DC bias.
diameter) stencil onto printed circuit board (PCB with current collectors). The printed carbon ink paste electrodes were cured for 60 min at 80 °C, followed by coating insulation ink (Ercon R-486(AH) Blue) on top of current collectors and then curing in oven again for 60 min at 80 °C.

Electrochemical deposition of polypyrrole was performed in solution containing 10 mM pyrrole and 10 mM PBS by cyclovoltammetric (CV), galvanostatic deposition at constant current and potentiostatic deposition at constant potential, respectively.

3. Results and discussion

3.1. Effect of deposition methods on polypyrrole films

CV, galvanostatic and potentiostatic depositions were carried out to investigate the effects of deposition methods on properties of polypyrrole thin films. The thickness of polypyrrole is determined by the electric charge passed during the electrochemical polymerization [8]. The film thickness was made identical to each other for comparison by controlling the same electric deposition charge of 0.42 C/cm². All investigation works on deposition methods were done with glassy carbon electrodes. The CV was conducted over potential range of −0.20 to 1.02 V vs. Ag/AgCl at scan rate of 100 mV/s for five cycles. Polypyrrole depositions with galvanostatic and potentiostatic methods were conducted at 0.25 mA/cm² for 2 min and at 0.8 V vs. Ag/AgCl for 100 s, respectively. After deposition, CV in 0.1 M PBS solution was performed to characterize the electrochemical reactivity of the polypyrrole films made from three different deposition methods. The results are shown in Fig. 1.

Electrochemical reaction activity of an electrode material is the most critical parameter for applications in energy storage systems and electrochemical sensors. In a CV, the higher the redox peaks, the greater the electrochemical reaction activity. Apparently, the galvanostatically deposited polymer film had the highest redox peaks, indicating the greatest electrochemical activity, and the potentiostatically deposited film had the worst redox capacity.

3.2. Impedance response vs. frequency on polypyrrole films

Impedance spectroscopy is an effective method for characterizing the interfacial properties of electrodes. The complex impedance can be presented as the sum of the real, $Z_{re}$, and imaginary, $Z_{im}$ components that originate mainly from the resistance and capacitance of the cell, respectively. A plot of $Z_{im}$ vs. $Z_{re}$ over frequencies in terms of impedance measurements, called as Nyquist diagram, is the powerful tool to evaluate an electrochemical system. Fig. 2 shows impedance results measured in 0.1 M PBS solution at galvanostatically deposited polypyrrole films on DuPont 7012 carbon composite electrodes with different DC bias vs. Ag/AgCl, but with the same ac amplitude of 10 mV. In Fig. 2, Nyquist diagrams include a semicircle region lying on the $Z_{re}$ axis followed by a straight line. The semicircle part, observed at higher frequencies, as well-known in literatures [11], corresponds to the electron transfer process, in which the radius of the semicircle is called Faraday resistance, whereas the linear part is characteristic of the lower frequencies range and represents the diffusion-controlled electrode process. However, the smaller the radius of the semicircle, the lower the Faraday resistance and the faster the electrochemical reactions. All Nyquist diagrams obtained with different electrodes including glass carbon, gold, and carbon composite electrodes demonstrated the same trend as the typical curve shown in Fig. 2, indicating that more positive bias had lower Faraday resistance. This showed that the polypyrrole films deposited on carbon composite electrodes made from carbon inks had the same electrochemical behavior as gold and glass carbon electrodes. For a conjugative conductive polymer, the redox

![Figure 3](image-url)
reaction comes from the anions doping/undoping process. The results further indicated that polypyrrole films deposited on different electrodes are p-type conjugative polymer, and can become more conductive and more electrochemically active at more positive polarization in an anodic process.

3.3. Stability of polypyrrole films on different substrate electrodes

In this study, all polypyrrole films were formed by galvanostatic deposition at constant current of 0.25 mA/cm². The main parameters of the carbon composite electrodes made from carbon inks are shown in Table 1. The instability of polypyrrole films in aqueous solution is mainly from solution attack, resulting in possible oxidation and swelling for film degradation. The stability experiments were conducted by soaking the deposited polypyrrole films in 0.1 M PBS solution, and impedance measurements were performed in 0.1 M PBS solutions at the start and end of the electrode soaking. Since the sizes of glass carbon and gold electrode (3-mm diameters) are much larger than that of screen-printed carbon composite electrodes (100-μm diameter) and the sizes of screen-printed electrodes had variations from each other, the impedance measured was normalized as change ratio of impedance measured at the end of the soaking to that measured at the start of the soaking for comparison.

The results of resistance measured at 100 Hz at different electrodes are shown in Fig. 3, which demonstrates that the stability of polypyrrole films on carbon composite electrodes made from DuPont’s inks were better than glass carbon, gold and Asahi carbon ink-made composite electrode. Carbon composite electrodes were rougher and had much higher specific surface area than glass carbon and gold electrodes. This might make the stability of polypyrrole films on the DuPont carbon surface better than the smooth electrode surface of glassy carbon and gold electrodes since roughness and large surface area could enhance adhesion and enforce the structure of polypyrrole film for stability. TU-158 carbon used different binder from DuPont 7012 and 7015. The binders could possibly affect the polypyrrole properties of electrode substrate materials affect the stability of polypyrrole films.

The relationship of stability of polypyrrole films on the electrode surface vs. testing frequencies was investigated. The resistance change of polypyrrole films on DuPont 7012 carbon electrode surface was measured after overnight immersing in 0.1 M PBS solutions, and the results were plotted as resistance change vs. frequency as shown in Fig. 4. The results demonstrate that there was no significant resistance change overnight in 0.1 M PBS from 1 MHz down to 10 Hz, and the resistance change sharply increased below 10 Hz. The results show that the instability occurred at lower frequencies. The resistance at lower frequencies represents the electron diffusion process in the polypyrrole films. In terms of these results, we would suggest that that the solution attack did not change the backbone of the conjugative polymer film to affect its doping process, but possibly partially isolated electronic communications between polymer molecules to limit the electron diffusional process in the polypyrrole films.

4. Conclusion

The results show that galvanostatic deposition of polypyrrole film could produce highest electrochemical reactivity in comparison to cyclic voltammetry and potentiostatic deposition methods, the conductive films on all substrates exhibited p-type conjugate polymer characteristics, and different electrode substrate materials have influences on stability of electrochemical polypyrrole thin films deposited on different substrates. The results also demonstrate that instability might be caused by partially isolation of electronic communication between polypyrrole molecules for limiting the diffusional electron transferring process. The study demonstrates the feasibility of using carbon ink to make composite carbon electrodes in sensor and energy storage system applications.

References