Electrodeposition of PPy/HNO₃ Film and its Capacitive Behaviour

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Abstract. Through cyclic voltammetry polypyrrole/nitric acid (PPy/HNO₃) film was electrodeposited on stainless steel mesh. Its special structure like corals was demonstrated by scanning electron microscopy (SEM). Various approaches such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectrum (EIS) were employed to investigate the electrochemical performance of PPy/HNO₃ film. The results showed that the specific capacitance of PPy/0.5M HNO₃ can reach to 596 F·g⁻¹ at a current density of 5 mA·cm⁻²; even 1000 cycles the specific capacitance still maintained 96% at a scan rate of 50mV·s⁻¹. All data illustrate that PPy/HNO₃ film may become a promising candidate for supercapacitor applications.

1. Introduction

Supercapacitors, featuring excellent power density, long cycling life and fast rate of charge–discharge, become more important category of energy storage devices than rechargeable batteries and conventional capacitors [1, 2]. As we all known that one of crucial factors determining the supercapacitor performance is electrode materials where transition metal oxides, carbon materials and conducting polymers are commonly used. Among these materials, PPy has attracted more attentions in view of its high conductivity, high specific capacitance (SC) and low cost [3].

Usually, two methods including electrochemical and chemical polymerization can be used to synthesize PPy[4]. In terms of polymer films, electrodeposition is a better preparation way in solutions containing pyrrole monomer. However, most investigations prove that PPy exhibits poor SC without dopants because the high SC of PPy largely depends on the doping/dedoping process of dopants that allows the charge storage in the material[5]. Therefore, many inorganic and organic acids are employed as dopants during polymerization process. For instance, Zhang et. al.[6] prepared PPy film on the stainless steel electrode via pulse galvanostatic method, and the specific capacitance was 403 F·g⁻¹ when p–toluene sulphonic acid was used as dopants. Furthermore, high active PPy owned SC of 480 F·g⁻¹ was electrodeposited on Ti foil by using oxalic acid as dopants through cyclic voltammetry at a scan rate of 200 mV/s[7]. R. Ramya et. al. [8] employed p-toluene sulphonic acid as dopants to synthesize PPy on stainless steel electrode via the galvanostatic polymerization, and SC of 200 F·g⁻¹ was achieved at 0.8 mA·cm⁻². X. Li[9] electrodeposited PPy films with 5-sulfosalicylic acid (SSA) as dopants on stainless steel substrates by galvanostatic and pulse method, and 545 F·g⁻¹ was the highest SC obtained at a scan rate of 2 mV·s⁻¹. Unfortunately, up to now, the SC of PPy reported by literatures is lower than the theoretical value(620F·g⁻¹) [10]. Thus, more efforts are on the way to enhance the electrochemical property of PPy.

In this work, HNO₃, one of inorganic acids, was utilized as not only electrolyte but also dopants to
fabricate PPy films on low cost stainless steel mesh substrates by cyclic voltammetry. As expected, a SC as high as 596 F·g⁻¹ can be provided by the PPy films at a current density of 5 mA·cm⁻², which is higher than above reported literatures.

2. Experimental

Pyrrole was purified before use. Electropolymerization was carried out on CHI660B electrochemical work station by using HNO₃ with different concentration of 0.1, 0.3, 0.5, 0.7 and 0.9 M, containing 0.1M pyrrole monomer. During electrodeposition, a standard calomel electrode(SCE) was used as reference electrode, and counter electrode and working electrode were supported by two stainless steel(316L,1×1cm), respectively. At a scanning rate of 5 mV·s⁻¹, 31 segments CV curves were performed to obtain the PPy films under the scanning potential from -0.2 to 0.9 V. After that, 0.5 mol·L⁻¹ HNO₃ and distilled water were used to rinse the deposited PPy films to remove the soluble species. Then, the obtained PPy films were dried for 12h at 60 ºC

The samples used in all tests were scraped from stainless steel mesh substrates. Scanning electron microscopy (SEM: J EOL JSM-6701F) was utilized to characterize the morphology of PPy films. The electrochemistry properties of samples were conducted in 0.5M H₂SO₄ electrolyte with a SCE electrode as the reference electrode and a platinum sheet as the counter electrode. The potential window was chosen between -0.3 and 0.7V when cyclic voltammograms(CV) and galvanostatic charge–discharge (GCD) were tested. Electrochemical impedance spectra (EIS) were recorded with the frequency ranging from 10⁵ to 10⁻² Hz under the amplitude of 0.5mV.

3. Results and Discussion

Figure 1 shows the relationship of deposition yield of PPy films and the concentration of HNO₃. It can be seen that the deposition yield increases with an increase of H⁺ concentration at the beginning, because the higher acidity the solution, the higher protonation degree of pyrrole. It suggested that H⁺ played an important role during the electrochemical polymerization of PPy[12]. However, with the further increasing of H⁺ concentration, the deposition yield is decreased, which is contributed to the decline of doping amount and the hydrolyzation of PPy. The morphology of PPy films is displayed in Figure 2. Obviously, PPy films exhibit coralline structure, which looks like an aggregation of PPy particles. The structure makes material loose and porous, benefitting for the improvement of its SC.

CV curves of PPy with different concentration of HNO₃ are depicted in Figure 3(A) at a scan rate of 5mV·s⁻¹ in 0.5M H₂SO₄ electrolyte between -0.3 and 0.7V. It is evident that the PPy films show good capacitive behavior, as indicated by distorted box shape CVs without obvious redox peaks. Furthermore, it is obviously observed that the area of CV curve of PPy/0.5M HNO₃ is much larger than others, implying the existence of a higher SC. At the same time, the conclusion can be proved by GCD test at current density of 5mA·cm⁻², which is presented in Figure 3(B). It is easily found that the shape of all lines are bended seriously rather than ideal straight lines, which derives from the faradic reaction between the surface of electrode and the electrolyte. The following equation is used to calculate the specific capacitance (Cₘ) of PPy films according to the discharge time in the GCD curves[13].

\[
C_m = \frac{I\Delta t}{m\Delta V}
\]

Where Cₘ(F·g⁻¹), I(A), Δt(s) and ΔV(V) represent specific capacitance, charge/discharge current, the discharge time and the potential drop in the discharge process, respectively. m(g) obtained by subtraction method is the mass of active material. Therefore, the correspondingly calculative results of SC of PPy films are attributed to 93, 355, 596, 242 and 135 F·g⁻¹ with the HNO₃ concentration of 0.1, 0.3, 0.5, 0.7 and 0.9M, respectively. Obviously, the highest SC of 596 F·g⁻¹ of PPy film is obtained in 0.5 M HNO₃, which is in accordance with the result of CV test.
Figure 1. Deposited mass of PPy on stainless steel.

Figure 2. SEM image of PPy film prepared in 0.5 M HNO₃.

Figure 3. (A) CV curves of PPy/HNO₃ films at a scan rate of 5mV·s⁻¹. (B) Charge–discharge curves of PPy/HNO₃ films at current density of 5mA·cm⁻². (C) EIS of PPy/HNO₃ films.

Only having the analyses of CV and GCD is not enough to estimate the electrochemical properties of PPy films. Another indispensable approach is EIS test, which can offer more information about charge-discharge kinetics. As is well-known, the curves are usually composed two parts in different frequency region, one is a semicircle, the other is a tilted straight line. Through the intercept of the semicircle on the real axis in high frequency, we can easily tell the solution resistance. Accordingly, the diameter of the semicircle directly points out the charge transfer resistance (Rct) that exists on the electrodes/electrolyte interface. Moreover, in low frequency region the tilted straight lines are used to verify a limiting diffusion process that happens in electrolyte to explain the behavior of ideal
capacitive[14]. The Nyquist plots of all samples are shown in Figure 3(C). We can clearly observe that the film prepared in 0.5 M HNO$_3$ have a smaller charge transfer resistance and nearly vertical line, which is beneficial for capacitive behaviour.

![Figure 4](image)

**Figure 4.** Specific capacitance versus cycle numbers at a scan rate of 50 mV·s$^{-1}$ (insert depicts the difference of CV curves of first cycle and 1000th cycle).

Another important indicator to use as electrodes in supercapacitor is the cycle stability of materials. Employed voltammetric cycles, we evaluated the cycle stability of PPy films in 0.5M HNO$_3$ solution. It can be seen in Figure 4 that an obvious decrease of specific capacitance that tied with the degradation of incompletely formed polymer or some un–doped PPy, occurs at the beginning, after that increase slightly because of the changes of electrode microstructure[15]. After 1000 cycles, a decrease of only 4% of the SC is observed, in other words, the SC still remains 96% of the initial value, indicating a good cycling stability. Moreover, the shapes of the 1st and the 1000th CV curves are similar each other, which can be observed in the inset in Figure 4.

**4. Conclusions**

Polypyrrole films with a high-performance were successfully synthesized by the cyclic voltammetry technique in nitric acid solution. It was found that, during the electrodeposition process, the nitric acid not only provides a acidic condition, but also employs as dopant ions, which is favourable to improving electrochemical properties of PPy. When the concentration of HNO$_3$ is 0.5 M, the highest specific capacitance was reached to 596 F·g$^{-1}$ at a current density of 5 mA·cm$^{-2}$. Furthermore, a decrease only 4% of the specific capacitance was observed after 1000 cycles. Therefore, a conclusion can be drawn that the PPy films deposited on low cost stainless steel substrates are excellent candidates for the electrode of supercapacitors.

**5. Acknowledgements**

This work was supported by the National Natural Science Foundations of China (51503092) and the Natural Science Foundation of Gansu Province (2017GS10857).

**6. References**

[1] Gogotsi Y, What nano can do for energy storage, 2014 Acs Nano 8 5369-71.
[2] Liew S Y, Thielemans W and Walsh D A, Electrochemical Capacitance of Nanocomposite Polypyrrole/Cellulose Films, 2010 Journal of Physical Chemistry C 114 17926-33.
[3] Lou X W, Deng D, Lee J Y, Feng J and Archer L A, ChemInform Abstract: Self-Supported Formation of Needlelike Co3O4 Nanotubes and Their Application as Lithium-Ion Battery Electrodes, 2008 Advanced Materials 39 258-262.
[4] Chen S and Zhitomirsky I, Capacitive behaviour of polypyrrole, prepared by electrochemical and chemical methods, 2014 Materials Letters 125 92-95.
[5] Khomenko V, Frackowiak E and Béguin F, Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations, 2005 Electrochimica Acta 50 2499-2506.

[6] Zhang J, Kong L B, Li H, Luo Y C and Kang L, Synthesis of polypyrrole film by pulse galvanostatic method and its application as supercapacitor electrode materials, 2010 Journal of Materials Science 45 1947-54.

[7] Fan L Z and Maier J, High-performance polypyrrole electrode materials for redox supercapacitors, 2006 Electrochemistry Communications 8 937-40.

[8] Ramya R and Sangaranarayanan M V, Analysis of polypyrrole-coated stainless steel electrodes—Estimation of specific capacitances and construction of equivalent circuits, 2008 Journal of Chemical Sciences 120 25-31.

[9] Li X and Zhitomirsky I, Capacitive behaviour of polypyrrole films prepared on stainless steel substrates by electropolymerization, 2012 Materials Letters 76 15-17.

[10] Liu A S and Oliveira M A S, Corrosion control of aluminum surfaces by polypyrrole films: influence of electrolyte, 2007 Materials Research 10 205-209.

[11] Roberts M E, Wheeler D R, Mckenzie B B and Bunker B C, High specific capacitance conducting polymer supercapacitor electrodes based on poly(tris(thiophenylphenyl)amine), 2009 Journal of Materials Chemistry 19 6977-79.

[12] Mandić Z, Duić L and Kovačiček F, The influence of counter-ions on nucleation and growth of electrochemically synthesized polyaniline film, 1997 Electrochimica Acta 42 1389-1402.

[13] Zhang J, Kong L B, Wang B, Luo Y C and Kang L, Electrochemical polymerization of polyaniline doped with Zn2+ as the electrode material for electrochemical supercapacitors, 2014 Journal of Solid State Electrochemistry 18 813-19.

[14] Wei H, Zhu J, Wu S, Wei S and Guo Z, Electrochromic polyaniline/graphite oxide nanocomposites with endured electrochemical energy storage, 2013 Polymer 54 1820-31.

[15] Shi K and Zhitomirsky I, Influence of current collector on capacitive behavior and cycling stability of Tiron doped polypyrrole electrodes, 2013 Journal of Power Sources 240 42-49.