

Research on interfacial polymerization of pyrrole assist with Span80 system

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Abstract. With assistance of surfactants, self-assembled Polypyrrole (PPy) film was prepared via oil / water interfacial polymerization. The chemical structure and morphologies of the obtained samples have been characterized by Fourier transform infrared (FT-IR) and Scanning Electron Microscope (SEM), respectively. The electrochemical performance recorded on an electrochemical workstation, mainly includes cyclic voltammetry (CV) tests. The prepared PPy film has its own extremely vesicular structures from results and indicates by using different concentration surfactant Span80. The PPy film prepared 25 °C with 3.32 g/L Span80 (surpass its critical micelle concentration) as a surfactant possess a supernal specific capacitance of 368.18 F/g at a scan rate 50 mV/s in 1 M NaNO₃ aqueous solution at.

1. Introduction

Recent advances in the field of electrically conducting polymers have aroused substantial scientific and technological interest to research the conducting polymers which characterized with increasing interests in the control of their morphology at the different level. Conductive polymers are prospective substitution for extensive applications in electrochemical energy storage devices, like sensors, energy storage, electrocatalysis, electrorheology, electromagnetic interference shielding, and biomedicine, or in the conversion to nitrogen-containing carbon materials [1-7] and so forth. Among them, polypyrrole (PPy) received much concern lied in its environmentally friendly, preferable electrical conductivity and relative ease of synthesis [8-10]. The polymerization method of polypyrrole involves the electrochemical process of oxidation and reduction [11]. Sahoo et al. [12] choose a facile route to synthesize a nanocomposite which based on graphene and Polypyrrole nanofiber. The maximum capacitance of this composite was 466 F/g and also presented the highest energy density of 165.7 Wh/Kg at 10 mV/s scan rate in 1 M KCl solution. Pierce et al. [13] deposited pyrrole on the surface of graphene oxide (GO) platelets with ammonium persulfate (APS) as an oxidant, generated PPy/GO hybrid assemblies, offered a way to generate new solid hybrids and change the physical properties systematically. Our laboratory [14] used FeCl₃ as oxidants, Tween80 as a surfactant to polymerize polypyrrole by interfacial polymerization; an optimized specific capacitance of 261 F/g can be obtained at scan rate 50 mV/s and retains 75% of the initial specific capacitance value after 1000 cycles.

In consideration of the pre-existing achievements, we know surfactants can form micelles that act as a template for synthesizing porous materials. So we choose long-chain surfactants Span80 to assist the polymerization of polypyrrole with particular morphology. The optimal PPy film presented improved specific capacitance in 1M NaNO₃ aqueous solution. The impacts of surfactant



concentration on the microstructure and surface morphology and faradaic pseudocapacitance behavior of as-prepared PPy films were explored.

2. Experimental

2.1. Reagents

Pyrrole was bought from Shanghai Sinopharm Chemical Reagent, purified by distillation under reduced pressure and stored in a refrigerator not exceeding 4 °C prior utilization. FeCl₃ was pure analysis and purchased from Tianjin Fuchen chemical reagents factory; Span80 was analytically pure and obtained from Tianjin Fuchen chemical reagent company; Hydrochloric acid (HCl), which was bought from Xian city west new fine chemical industry.

2.2. Preparation of PPy

Polypyrrole (PPy) was prepared in chloroform (CHCl₃) / water interface and used FeCl₃ as oxidant via interfacial polymerization, and 0.52 ml pyrrole was dissolved in 50 ml chloroform (CHCl₃) solution which includes Span80 to develop the oil phase, and oxidant FeCl₃ is dissolved in deionized water to compose aqueous phase followed Table 1. With a glass rod making oxidant solution to drainage into the organic phase, form the interface. Polymerization conditions choose static interface react 5h at 25 °C, a black self-assembled polypyrrole freestanding film was displayed in interface. The synthetic samples was disposed with deionized water and ethyl alcohol for many times and dried in a vacuum oven for 24h at 60 °C.

Table1. Experimental formula of Span80 system.

Number	1	2	3	4	5
Span80 (g/L)	0	0.003	0.065	0.323	3.32

2.3. Characterization of PPy

We used SEM (JSM-6460LV, JEOL, and Japan) to observe the products micro morphologies. The FT-IR spectra were list on a Bruker FT-IR Equinox 55 spectrophotometer with KBr pellets. A total of scans arranges from 400 to 5000 cm⁻¹.

Cyclic Voltammetry (CV) Tests and Electrochemical Impedance Spectroscopy (EIS) detection were obtained by employing Model CS350 Electrochemical workstation (Wuhan, China) PPy was served as a working electrode. The counter electrode was platinum and the reference electrode was calomel electrode, respectively. The electrolyte is 1 M NaNO₃, CV tests were done between -0.4 and 0.6 V at a scan rate of 50 mV/s. EIS tests were carried out with an AC perturbation of 10 mV in the frequency range from 10⁵ to 0.01HZ at open circuit.

3. Results and discussions

3.1. Microstructure of PPy

The microstructure of PPy films is presented in Figure 1. They are corresponding to the samples of 1, 2, 4 and 5 in Table 1. PPy will express a micro globular together or spread and aggregation morphology clutter without surfactants added in Figure 1 a. The morphology of PPy will be mostly changed when Span80 added. A morphological structure with different vesicles of varying size existing, and they are merging to a certain content when the concentration of surfactants is high. What can explain the phenomena is that the concentration of Span80 addition surpassing the critical micelles concentration of Span80. The increased volume and numbers of micelles induce to the simple merging mutually. It follows that polypyrrole can be induced to grow in this model, like Figure 1 b and c. When the concentration of Span80 increasing sequentially, the micelle shape can be changed and result in granular PPy, and a relatively compact skeletal structure presented, as shown in Figure 1 d.

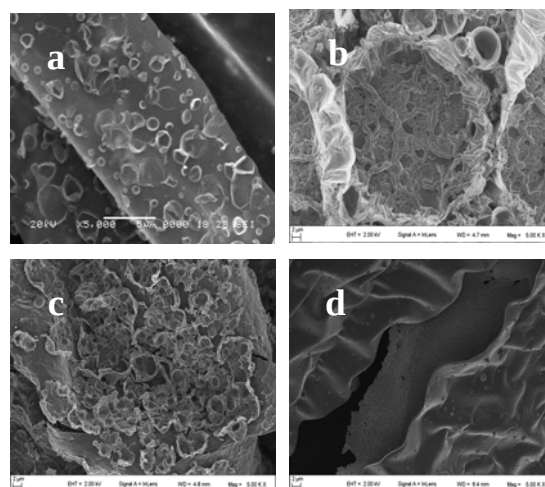


Figure 1. SEM images of PPy prepared with Span80 (a, b and c are corresponding to 1, 2, 4 and 5.).

As shown in Figure 2, the absorption peaks at 1400 cm^{-1} and 1540 cm^{-1} belong to the asymmetric and symmetric pyrrole ring-stretching modes, respectively. Peaks at 1300 cm^{-1} is associated with the C-N stretching vibration, 1041 cm^{-1} and 1138 cm^{-1} are ascribed to the =C-H in-plane vibration. Peaks at 905 cm^{-1} and 960 cm^{-1} are observed as PPy doping state respectively and the =C-H out-of-plane vibration, The N-H bond in-plane vibration showed at 781 cm^{-1} . Near infrared area, 3128 cm^{-1} is caused by the residual surfactant and hydroxyl of water. The shifting of the peaks indicates the change in the chemical environment during the formation of the samples. Thus, the FTIR results reveal the successful preparation of PPy.

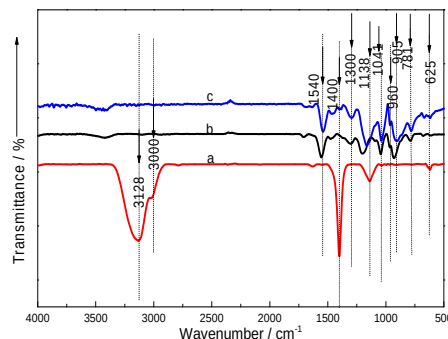


Figure 2. FTIR spectra of PPy (a, b and c are 1, 3 and 5).

3.2. Electrochemical Performance of PPy

Figure 3 reveals the CV curves of the specimen; line 1 displays the cyclic voltammetry curve of sample 1. All symmetric curves demonstrate the excellent reversibility of polypyrrole in a reasonable scanning stable potential. A rectangular shape is obviously different from the conventional conductive polymer, mainly depends on the amounts of chain segments participated in whole electrochemical reaction during the circular scanning process. The more chain segments take part in, the better rectangle shape present. According to the equation (1) [15], the specific capacitance of sample 1 obtained is 90.26 F/g . Because each of the polypyrrole chains can't for charge and discharge completely, a low active material utilization ratio during the cyclic voltammetry (CV) scanning process inducing a small specific capacitance. With the increasing of Span80 concentration, the cyclic voltammetry curve shape of the active materials changed observably and the trend of the curves show symmetrical distribution approximately, without any apparent oxidation and deoxidation peaks, corresponding to the flats of charge and discharge. It all comes to describe a stable exchange of electrolyte and electrode in the process of a given charging and discharging process, a higher

electrochemical reversibility, a fine supercapacitors electrode material properties emerging. The area results of oxidation and deoxidization curves confirm the value of the specific capacitance. The calculation of 2, 3, 4 and 5 are 132.75 F/g, 154.87 F/g, 220.13 F/g and 368.18 F/g. The calculations are respectively consistent with the galvanostatic charge-discharge test results we used later.

$$C_s = \frac{\int_{V_a}^{V_c} I(V) dV}{m \nu (V_c - V_a)} \quad (1)$$

Where C_s , I , m , and ν are the specific capacitance (F/g), sweep current (A/cm²), the mass of the active electrode materials (electrode area of PPy is about 1 cm², g), and voltage sweep rate (mV/s), respectively.

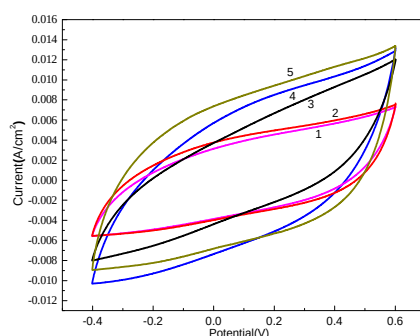


Figure 3. CV curves of PPy.

3.3. Conclusions

A non-ionic surfactant system was used, PPy electrode materials were prepared by interfacial polymerization, and the influence of synthesis conditions on PPy films performance was studied, then we come to the conclusion that the chemical composition of PPy can't be totally changed by adding Span80, but changed significantly in morphology. With increasing Span80 concentration, the morphology of PPy changed from disorderly deposits microspheres to vesicle accumulation formed, until a relatively compact skeletal structure presented at last. The electrochemical tests manifest the rising specific capacitance of PPy with adding Span80 increasing. When Span80 concentration is 3.32 g/L, we received optimized specific capacitance is 368.18 F/g.

Acknowledgments

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