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Pulse electrochemical incorporation of graphene oxide into polypyrrole films for supercapacitor electrode materials

Kai Qi[a], Yubing Qiu[a,*], Xingpeng Guo[a,b]

[a] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China
[b] Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, Wuhan 430074, PR China

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ABSTRACT

In order to synthesize a PPy/GO composite for supercapacitor applications, a pulse electro-polymerization method was proposed to direct incorporate graphene oxide (GO) into polypyrrole (PPy) films without any additional dopants. The PPy/GO prepared by the pulse electro-polymerization (PC PPy/GO) exhibits a higher specific capacitance. A shorter pulse on time (t_{on}) results in higher specific capacitance, but there is an optimum pulse current amplitude (I_A) related to the highest specific capacitance. The PC PPy/GO film ($I_A = 4$ mA cm^{-2}, $t_{on} = 50$ ms) has a high specific capacitance of 660 F g^{-1} estimated from galvanostatic charge-discharge in 1 M KCl at a current density of 0.5 mA cm^{-2}. Stability tests for the PPy/GO yield long cycling life up to 1000 cycles with 10% decay in specific capacitance at charge-discharge current density of 10 mA cm^{-2} in the potential range of -0.5 to 0.5 V_{SCE}.

1. Introduction

Polypyrrole (PPy) has been widely used as artificial muscles [1,2], sensors [3,4], catalysts [5–7], batteries [8] and protective coatings for metals [9–15], etc., owing to its advantageous physical and chemical properties, such as relatively high conductivity, novel electrochemical and optical properties, good biocompatibility and ease of synthesis by chemical or electrochemical methods [16–21]. Especially, PPy is a promising electrode modified material for supercapacitors due to its high pseudocapacitance, which stores electrical energy electrochemically by means of reversible faradaic redox reactions on the surface of suitable electrodes in an electrochemical capacitor with an electric double-layer, arising from the existence of redox states in the presence of dopants [22–24].

The capacitive performance of PPy is strongly dependent on its electronic/ionic conductivity, electrochemical reversibility, doping/dedoping processes and degradation behaviour, which may be impacted by the PPy structure [25]. Using composites of conductive polymers with carbon materials, including graphite, carbon fibers, carbon nanotubes, fullerenes, and graphene [26–30], is an effective method to improve the capacitance, conductivity and stability of PPy. In particular, graphene, a single layer of carbon atoms is an attractive electrode material for electrochemical energy storage for its high accessible surface area and conductivity [31]. Researches on graphene and its composites for supercapacitors have excited a lot of interest [32–35]. The specific capacitance value could be enhance from 108 to 289 F g^{-1} at a constant current density of 1 A g^{-1} through the electrochemical incorporation of GO in PPy film [36]. Other related research results are listed in Table 1 [36–42], which shows the specific capacitances and stability of various graphene (oxide) and PPy composites. Obviously, PPy and graphene composites are attractive for supercapacitor electrode materials.

Generally, electro-polymerized PPy shows higher electrical conductivity and more ordered PPy chain structures than that synthesized by chemical methods and therefore, the electro-polymerized PPy may be more suitable for supercapacitors. Moreover, several studies [43,44] indicate that pulse electro-polymerization methods can decrease the defects in PPy structure and improve its electrochemical performance, which suggests that the pulse electro-polymerized PPy may have better performance in supercapacitors.

In this paper, we prepare a PPy/GO composite using the pulse electro-polymerization method to incorporate GO into PPy without any other additional dopants in order to improve its capacitive property. The PPy/GO composite is characterised by Fourier transformed infrared (FTIR) and scanning electron microscopy (SEM). The electrochemical performance of the PPy/GO composite is measured by cyclic voltammetry (CV), electrochemical impedance spectrum (EIS) and galvanostatic charge-discharge methods. The effects of the on time and current amplitude of the pulse on the capacitance of the PPy/GO composite are also studied.

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* Corresponding author. Tel.: +86 27 87543432; fax: +86 27 87543632.
E-mail address: qiuyubin@mail.hust.edu.cn (Y. Qiu).

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Table 1
Specific capacitances of various graphene (oxide) and PPy composite electrode materials*.

Electrode materials	Electrolytes	Specific capacitance ($F\,g^{-1}$)*	Stability	Ref.
graphene/PPy	1 M H_2SO_4	424 (1 $A\,g^{-1}$)	–	[36]
graphene hydrogel/PPy	0.5 M H_2SO_4	348 (50 $mV\,s^{-1}$) 316 (5 $A\,g^{-1}$)	capacitance decreases 22% after -0.1 to 0.7 V at 5 $A\,g^{-1}$ for 4000 cycles	[37]
ethylene glycol reduced graphene oxide/PPy	1.0 M H_2SO_4	420 (0.5 $A\,g^{-1}$) 240 (5 $A\,g^{-1}$)	capacitance decreases 7% after -0.3 to 0.7 V at 1 $A\,g^{-1}$ for 200 cycles	[38]
exfoliated graphene/PPy-NDS	3 M KCl	351 (1 $A\,g^{-1}$)	capacitance decreases 18% after -0.8 to 0.5 V at 5 $A\,g^{-1}$ for 1000 cycles	[39]
graphene oxide/PPy nanowire	1 M KCl	695 (2 $mV\,s^{-1}$) 675 (2.5 $A\,g^{-1}$)	capacitance decreases 7% after -0.3 to 0.7 V at 50 $mV\,s^{-1}$ for 1000 cycles	[40]
graphene/PPy nanofiber	1 M KCl	466 (10 $mV\,s^{-1}$)	capacitance decreases 15% after -0.8 to 0.8 V at 10 $mV\,s^{-1}$ for 600 cycles	[41]
graphene nanosheets/PPy	1 M H_2SO_4	482 (0.5 $A\,g^{-1}$)	capacitance decreases 5% after -0.2 to 0.7 V at 50 $mV\,s^{-1}$ for 1000 cycles	[42]

*three electrode system

2. Experimental

2.1. Reagents and materials

Pyrrole (SAFC, 98+ %) used for the synthesis of PPy was distilled and kept refrigerated in the dark before use. Graphene oxide was synthesized from graphite powder with modified Hummer's method [45,46]. The desired amount of GO was added in deionized water and ultrasonication for about 1 h to form a uniform GO solution. Pyrrole was then added to the GO solution. Other reagents and chemicals were analytical reagents (AR) grade and used as received. Solutions were prepared with deionized water, and all experiments were carried out at an ambient temperature (22 ± 0.5 °C).

2.2. Preparation of the PPy/GO composites

All electrochemical experiments in this work were performed using a CHI660 C electrochemical workstation (Shanghai Chenhua Instruments, Inc., China) with a conventional three-electrode system in a single compartment cell. The counter and reference electrodes were a large Pt foil and a saturated calomel electrode (SCE), respectively. The working electrode for electropolymerization was a Pt plate (0.25 cm^2) that was sealed by epoxy resins, polished with a diamond polishing paste (the grain diameter is 0.5 μm), and rinsed in ethanol and distilled water. PPy/GO composites were electrochemically synthesized on the Pt plate electrode with pulsed currents (PC) in 0.2 M pyrrole + 5 mg mL^{-1} GO aqueous solutions (PC PPy/GO) which had been deaerated by bubbling pure N_2 gas for 20 min before synthesis. The waveform of the square wave pulsed current is schematically shown in Fig. 1, in which the on time (t_{on}) of the pulse current varies from 10 ms to 1000 ms while the off time (t_{off}) is constantly 300 ms and the current amplitude (I_A) is in the range of 1 to 8 mA cm^{-2}. Polymerization charge (Q_{poly}) was 800 mC cm^{-2} in every synthesis by controlling the total growth time (t_{growth}). For comparison, a PPy/GO was polymerized with a direct current (DC, 4 mA cm^{-2} for 200 s) in the same 0.2 M pyrrole + 5 mg mL^{-1} GO aqueous solution (DC PPy/GO), and a pure PPy film was also prepared by the pulsed procedure ($I_A = 4$ mA cm^{-2}, $t_{on} = 50$ ms, $t_{off} = 300$ ms) in 0.2 M pyrrole + 0.1 M KCl solution (PC PPy).

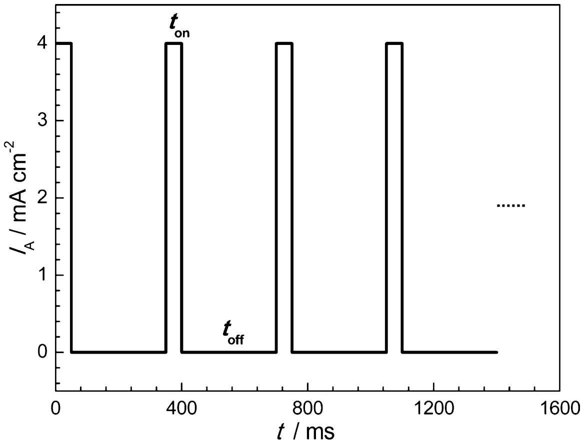

Fig. 1. Schematics of the pulse current waveform.

2.3. Characterization

The electrochemical tests were performed in 1 M KCl solution. CVs were performed in the potential range of -0.5 to 0.5 V_{SCE} with different scan rates, starting from the E_{OCP} towards negative direction, and 10 cycles were recorded. The amplitude of the AC perturbation in EIS was 5 mV and the frequency range was 100 kHz ~ 0.01 Hz. The galvanostatic charge-discharge was measured at different current densities in the potential range of -0.5 to 0.5 V_{SCE}. The specific capacitance (C, F g^{-1}) can be calculated from the charge-discharge curves according to Eq. (1),

$$C = (i\Delta t)/(m\Delta V) \quad (1)$$

where i (A) is the charging current, Δt (s) is the discharging time, m (g) is the mass of active composite material measured with an electronic analytical balance, and ΔV (V) is the voltage drop upon discharge.

The films were analysed using a Bruker Vertex 70 Fourier transformed infrared (FTIR) spectrophotometer in reflectance mode. The FTIR spectra were collected with a resolution of 4 cm^{-1}, and 64 scans were averaged for each sample. The images of surface and cross section of the films were observed on a FESEM instrument (JSM-6700F, Japan).

3. Results and Discussion

3.1. FTIR and morphology of PPy/GO composites

Fig. 2 shows the FTIR spectra of GO, PC PPy and PC PPy/GO ($I_A = 4$ mA cm^{-2}, $t_{on} = 50$ ms, $t_{off} = 300$ ms) composites. GO shows the characteristic absorption bands of oxide groups, such as the C=O peak at 1731 cm^{-1}, the peaks of O-H groups at 1417 cm^{-1}, and the C-O (alkoxy) peak at 1051 cm^{-1}. Compared with GO, several new peaks attributed to PPy appeared in the spectrum of PPy/GO. The new peaks at 1541, 1379, and 946/808 cm^{-1} are attributed to the C-C, C-N, and C-H groups in the PPy ring. It should be noted that the peak due to the C=O group within the PPy/GO composites has been downshifted to 1700 cm^{-1} which is probably due to the π-π interactions and hydrogen bonding between the GO layers and aromatic polypyrrole rings, indicating that the carboxyl groups from GO acted as efficient dopants in the polymerization [47].

The surface morphology of the PC PPy/GO film ($I_A = 4$ mA cm^{-2}, $t_{on} = 50$ ms, $t_{off} = 300$ ms) is shown in Fig. 3 (a) and (b). For comparison, the SEM images of the DC PPy/GO film are also shown in Fig. 3 (c) and (d). The thickness of the two PPy/GO films measured by SEM is around 2 μm, which is consistent with the calculated