

Electrochemical codeposition of graphene/polypyrrole composites on carbon paper for electrochemical capacitors



Yanhui Liu, Ke Xu^{*}, Xiaochen Zhang, Chunhua Qi, Qingchun Lv, Houjun Feng

The Institute of Seawater Desalination and Multipurpose Utilization, SOA, Tianjin 300192, PR China

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ABSTRACT

A simple electrochemical codeposition technique has been introduced to fabricate graphene oxide/polypyrrole (GO/PPy) composites. To increase the adsorption of colloidal GOs at the liquid–liquid interface, the organic supporting electrolyte like benzenesulfonate sodium (BS) is added in GO/pyrrole micelle solution, which does not induce the flocculation sedimentation of GO at elevated ionic strength. The narrow size distribution of GO/pyrrole/BS micelles is benefit for uniform codeposition of GO/PPy on the carbon fiber surface. Moreover, the GO nanosheets and benzenesulfonate have been incorporated into composites as mixture dopants, which increased the growth orientation of PPy in electropolymerization process and result in more loose structure for ionic transportation. The composites electrodes exhibit high specific capacitance, good cyclic stability after electrochemical reduction of graphene oxide (RGO). The specific capacitance of composite electrode with low mass density still reaches 358 F/g at scan rate of 10 mV/s within an electrochemical windows of 1.0 V. The strong interaction effect between two components resists the mechanical deformation effect and exhibits only 7.1% decay at a charge/discharge current of 3 A/g after 1000 cycles. At increasing the mass density of composites to 8.4 mg/cm², the areal capacitance of electrode almost grow linearly to 1.286 F/cm², which is more than triple that of BS-doped PPy with the same mass density. The high capacity of the composite electrode exerts the potential applications in capacitive deionization, microbial fuel cell or even capacitive energy storage.

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1. Introduction

Graphene has attracted much interest as a promising electrode material in capacitive energy storage [1–4], capacitive deionization [5–7] or even microbial fuel cell [8] owing to its high specific surface area and good conductivity. And composites of graphene with other pseudocapacitance materials, such as metal oxides and conducting polymer, have proved to be a kind of practical methods to combination of their intrinsic characteristic for developing high performance electrochemical capacitors [9–11]. These composites were shown to enhance charge density, electrical conductivity, and electrochemical redox activity compared with pseudocapacitance materials alone or graphene alone.

The electrochemical codeposition is a promising technique that offers the opportunity of obtaining graphene/conducting polymer composite electrodes with reliable electrical connection to the current collector and lower internal resistance than conventional

chemical method due to no polymeric binder in matrix of electrode. For example, Wang et al. used sodium p-toluenesulfonate to improved the dispersion stability of reduced graphene oxide (RGO) in electrolytes, and the specific capacitance of in situ electro-polymerized graphene/PPy composites (1 C/cm² polymerization charge) was 224F/g at charge/discharge current density of 240A/g [12]. Chang et al. used graphene oxide as supporting electrolytes and external dopant of PPy for avoiding coagulation of GO colloidal solution at elevated ionic strength [13], and this GO/polypyrrole could be electrochemical reduced for higher specific capacitance of 424F/g at current density of 1A/g [14]. However, when composite is densely electrodeposited on the current collector, the limited accessible surface area and ion migration is participated in electrochemical charge storage process, thus resulting in remarkably increasing the internal resistance and in turn decreasing the specific capacitance. Zhou et al. has extended the electrodeposition time for improved the areal capacitance of composite electrode, but only 152 mF/cm² is achieved at scan rate of 10 mV/s due to the limited diffusion of electrolyte ions [15]. Therefore, to maximize the utilization of GO/PPy composites for improving the areal capacitance, it is essential to introduce conductive three dimensional (3D) scaffold in composites, which provide not only high surface area for

^{*} Corresponding author. Department of Seawater Desalination, The Institute of Seawater Desalination & Multipurpose Utilization, SOA, Tianjin 300192, PR China.
E-mail address: xukeler@hotmail.com (K. Xu).

loading electro-active materials, but also high porosity and conductivity for facilitating the fast electron and ion transport throughout the matrix of electrode [16].

Herein, the surfactant nature of graphene oxide (GO) was utilized to adsorb and packet the pyrrole monomers in the micro-scale “GO cages” due to the intensive interaction effect and emulsification abilities of GO at the liquid–liquid interface [17]. And to avoid the inhomogeneity of electrolyte solution due to the coexistence of GO/pyrrole micelles and colloidal GO [18], the benzenesulfonate sodium (BS) was added and acted as interfacial tension regulator to improved the adsorption of GO at pyrrole droplet surface. Thus, the narrow size distribution of micelles can ensure the uniform growth of the GO/PPy composites on the porous carbon fiber substrates. The morphologies, electrochemical redox characteristic as well as the cycling stability of the composite electrodes were examined.

2. Experimental

2.1. Chemical and materials

The starting bare anode was a piece of porous carbon fiber paper (Toray Industries Inc., TGP-H-060) that has a dimension of $3\text{ cm} \times 1.5\text{ cm} \times 0.019\text{ cm}$. Prior to use, it was cleaned in a hot H_2O_2 (10%, $90\text{ }^\circ\text{C}$) solution for 3 h, followed by thorough rinse with deionized water and vacuum dry at $60\text{ }^\circ\text{C}$. GO prepared by a modified Hummers method were purchased from the Institute of coal chemistry, Chinese academy of science. Pyrrole (A.R.) was distilled prior to use and stored at $-10\text{ }^\circ\text{C}$ in a nitrogen atmosphere. Potassium chloride (A.R.) and benzenesulfonate sodium (C.P.) were used as received.

2.2. Composites electrode preparation

The freshly distilled pyrrole (335 mg) was added into 50 mL GO colloid solution with concentration of 0.3 mg/mL, and stirred rapidly for 4 h to form GOs caged pyrrole solution. After that, the different amount of benzenesulfonate sodium was added and stirred for 1 h to control the size distribution of GO/pyrrole micelles. Finally, the pH value of the solution was adjusted to 3 by using benzenesulfonate. The size and distributions of GO/pyrrole micelles were determined by laser diffraction using a Malvern Mastersizer 2000. And the optical micrographs of micelle was obtained by using a Leica DM2500 M microscope.

Electrochemical polymerizations were all performed by a galvanostatic method in three-electrode cell equipped with a carbon fiber papers as the working electrode (anode projected surface area of 4.5 cm^2), a platinum sheet as the counter electrode and a standard calomel electrode (SCE) as the reference electrode. The deposition current density was 2 mA/cm^2 , the polymerization charge was from 0.5 C/cm^2 to 20 C/cm^2 respectively. After that, the reduction of GO-based composite electrode was performed by scanning the potential from 0 to -1.0 V (vs. SCE) in 1.0 M KCl . All of the electrochemical operation were conducted on PARSTAT 2273 electrochemical station (Princeton Applied Research). All the solutions were degassed with nitrogen gas for 30 min before used, and a nitrogen atmosphere was kept during the solution preparation, electropolymerization and electro-reduction processes.

2.3. Material characterization

The microstructure of the GO-based composites and BS-doped PPy were investigated on a FEI Quanta 200 scanning electron microscope (SEM) operated with a voltage of 20.0 kV . Electrochemical capacitive behavior of composites electrodes were investigated in 1 M KCl aqueous solutions. The EIS were measured using 5 mV AC

sinusoid signal and at a frequency range from 100 kHz to 0.01 Hz at the open circuit potential. Cyclic voltammetry (CV) studies were performed within a potential range of -0.5 to 0.5 V versus SCE at scan rates of 5 – 100 mV/s . The specific capacitance (SC) was calculated using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the composite mass (m) and the potential window (ΔV):

$$C = Q/(m \cdot \Delta V) \quad (1)$$

The areal capacitance (C_s) of composite electrodes can be calculated based on CV curves according to following Eq. (2):

$$C_s = Q/(S \cdot \Delta V) \quad (2)$$

where S is the surface area of active materials in the single electrode in cm^2 .

The cyclic stability was measurements by galvanostatic charge/discharge technique with current density of 3 A/g . The specific capacitance of the composite electrode was calculated by using the Eq. (3):

$$C = (i \cdot t)/\Delta V \quad (3)$$

where i is the discharge current density in A/g , t the discharge time in s, and ΔV the scan potential window in V.

3. Results and discussion

3.1. Effects of benzenesulfonate on the size of GO/pyrrole micelles

GO nanosheet is composed of a 2D lattice of partially broken sp^2 -bonded carbon networks with phenol, hydroxyl, epoxide groups on the basal planes and carboxylic acid groups at the edges, which make it having amphoteric (hydrophilic–hydrophobic) properties like conventional organic surfactant molecule, and can be used to stabilize the oil-in-water emulsions [19]. Thus, mixing the GO colloidal solution with pyrrole monomers could also form the o/w micelles, and the measured size distribution of micelles was shown in Fig. 1. The light-scattering distribution of GO/pyrrole micelles was multi-modal, with the first peak between 40 and 550 nm , the second peak between 1.7 and $30\text{ }\mu\text{m}$, and the third peak between 30 and $160\text{ }\mu\text{m}$. The size distribution of first peak is

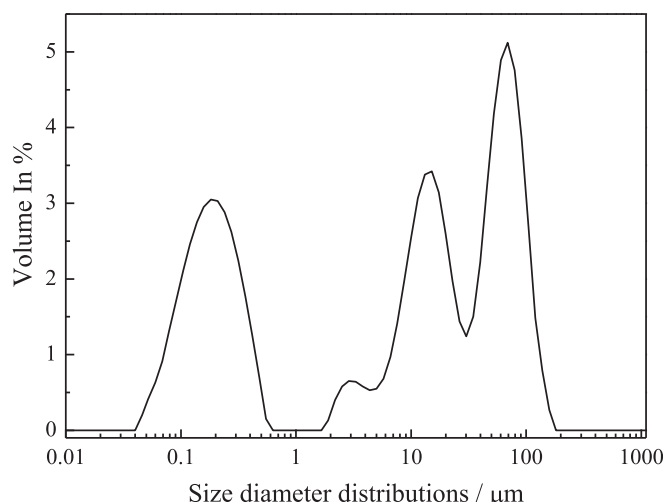


Fig. 1. Size diameter distribution of GO/pyrrole micelle system after dilution.

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