Journal of Power Sources 329 (2016) 516–524

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Freestanding hierarchically porous carbon framework decorated by polyaniline as binder-free electrodes for high performance supercapacitors

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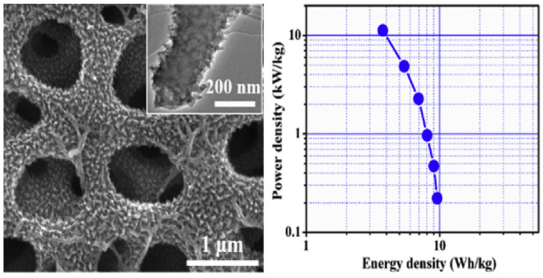
HIGHLIGHTS

- Hierarchically porous carbon can be facilely prepared by a template-free method.
- The HPC/PANI composites present high capacitance and rate capability.
- The as-assembled HPC/PANI-based device also exhibits good capacitive performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form
21 August 2016
Accepted 26 August 2016
Available online 2 September 2016

Keywords:
Carbon materials
Hierarchical porosity
Polyaniline
Freestanding
Supercapacitors

ABSTRACT

Freestanding hierarchically porous carbon electrode materials with favorable features of large surface areas, hierarchical porosity and continuous conducting pathways are very attractive for practical applications in electrochemical devices. Herein, three-dimensional freestanding hierarchically porous carbon (HPC) materials have been fabricated successfully mainly by the facile phase separation method. In order to further improve the energy storage ability, polyaniline (PANI) with high pseudocapacitance has been decorated on HPC through in situ chemical polymerization of aniline monomers. Benefiting from the synergistic effects between HPC and PANI, the resulting HPC/PANI composites as electrode materials present dramatic electrochemical performance with high specific capacitance up to 290 F g^{-1} at 0.5 A g^{-1} and good rate capability with ~86% (248 F g^{-1}) capacitance retention at 64 A g^{-1} of initial capacitance in three-electrode configuration. Moreover, the as-assembled symmetric supercapacitor based on HPC/PANI composites also demonstrates good capacitive properties with high energy density of 9.6 Wh kg^{-1} at 223 W kg^{-1} and long-term cycling stability with 78% capacitance retention after 10 000 cycles. Therefore, this work provides a new approach for designing high-performance electrodes with exceptional electrochemical performance, which are very promising for practical application in the energy storage field.

1. Introduction

Supercapacitors as advanced energy-storage devices have achieved a considerable interest and attention due to their high power density, long cycling life and rapid charge-discharge rate [1,2]. The realization of supercapacitors with high capacitive performance

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http://dx.doi.org/10.1016/j.jpowsour.2016.08.111
0378-7753/

strongly depends on the electrode materials [3]. Among various supercapacitor electrode materials, carbon-based electric double layer capacitors (EDLCs) store charges depending on purely electrostatic in nature, always suffering from low energy density [4,5]. In contrast, transitional metal oxides/hydroxides or conducting polymers based pseudocapacitors store charges by a Faradaic reaction as a charge-transfer reaction occurring between the interfaces of electrode-electrolyte, successfully achieving high energy density [6–8]. Compared to the transitional metal oxides/hydroxides with bad conductivity, polyaniline (PANI) with the advantages of good electrical conductivity and multiple intrinsic redox states leading to high specific capacitance and good rate capability, has attracted much attentions as the electrode materials for pseudocapacitors [9,10]. However, the unfavorable kinetics and underutilization of PANI in the charge-discharge process greatly reduces the rate capability and reversibility. Furthermore, the volume change of PANI caused by extraction/insertion of ions during the charge-discharge process also leads to the structural destruction and instability, which further hinders the practical application as electrode materials for supercapacitors [11,12]. In order to solve these problems, nanostructuring PANI can effectively shorten the ion diffusion length as well as achieve fast collect/transport of electrons from PANI to the substrate. Consequently, depositing PANI onto an appropriate nanostructured substrate demonstrates to be a promising approach to provide both the increased electron conductivity and reinforcement structural stability of PANI [9,11].

Carbon materials with the advantages of various nanostructures, good chemical/physical stability, light weight, large surface areas, and good conductivity have long been considered as ideal substrates for PANI deposition. In fact, many studies have been conducted and achieved good capacitive performance by incorporating PANI with different carbon materials including 0-dimensional active carbon [13,14], 1-dimensional carbon nanofiber or carbon nanotube [15,16], 2-dimensional graphene [11] and 3-dimensional porous carbon [17]. It is well known that PANI well-dispersed on these carbon materials can effectively avoid itself agglomeration and increase the accessible surface area with electrolyte. Moreover, the carbon materials as substrate can also facilitate fast transport/collect of electrons from PANI to carbon substrates as well as to the current collectors [18–20]. Thus, depositing PANI onto carbon substrates contributes to the realization of high capacitance and rate capability for PANI-based supercapacitor electrodes. Currently, most of the investigated PANI-based electrode materials are in powder form leading to that the traditional slurry-derived electrode preparation has to be employed during the supercapacitor electrode preparation [11–13]. It is widely accept that the polymer binder adding during the electrode preparation always results in large contact resistance and “dead volume” for the electrode active materials, limiting the enhancement of capacitive performance. Inspired by this, developing freestanding carbon substrates for PANI can effectively avoid the polymer binder adding as well as simplify the preparation procedure of supercapacitor electrodes [20,21]. Most importantly, the freestanding electrodes with continuous conductive backbones can greatly reduce the internal resistance and accelerate the electron transport. Moreover, if the carbon substrate with large surface areas and hierarchical porosity can further increase the electrode-electrolyte interface area as well as facilitate ion diffusion rate, further improving the capacitive performance [22–24]. Thus, the fabrication of freestanding hierarchically porous carbon substrates presents great significance to the high-performance supercapacitors [25,26]. To date the hierarchically porous carbon materials have been widely prepared through different methods such as directly carbonizing carbon precursors, template-guided methods (zeolites, silica or AAO template), hydrothermal treatment, ice-templating or freeze-casting, etc [27]. However, the as-synthesized porous carbon materials are always lack of free-standing nature and sometimes involve expensive sacrificed scaffolds, harsh experiment conditions or cost/time-consuming synthetic process, which actually can't meet the requirement for large-scale preparation for practical application. On the basis of above, the fabrication of freestanding hierarchically porous carbon substrate via a controllable and scalable method is still a significant challenge. Therefore, it is highly desirable to develop a simple and versatile template-free synthesis method to prepare the free-standing hierarchically porous carbon substrates for PANI depositing to achieve high capacitive properties.

Herein, developed phase separation induced by immersion precipitation method was carried out to prepare the freestanding hierarchically porous carbon (HPC) materials, which has been demonstrated to be a very effective approach [28,29]. In brief, the viscous precursor solution of polyvinyl pyrrolidone (PVP), polyacrylonitrile (PAN) and dimethyl formamide (DMF) in the presence of water would cause a phase separation among the precursor polymers and result in freestanding PAN membrane with highly uniform and well-interconnected porosity. By carbonizing the obtained PAN membrane at high temperature under nitrogen atmosphere, the final HPC materials could be easily prepared which still well maintained the initial freestanding nature and porosity architecture. Moreover, the obtained HPC also achieved other favorable features of large accessible surface areas and three-dimensional highly conductive cross-linked carbon backbones, which would be an ideal support for PANI depositing to fabricate HPC/PANI composites by in situ chemical polymerization. As expected, benefiting from the synergistic effects among these favorable features, the as-prepared HPC/PANI composites as supercapacitor electrodes have presented excellent electrochemical performance with high specific capacitance of 290 F g^{-1} at 0.5 A g^{-1} and high rate capability with ~86% (248 F g^{-1}) retention at 64 A g^{-1} of initial capacitance. Furthermore, the as-fabricated symmetric supercapacitor based on HPC/PANI composites also demonstrated good capacitive properties with a maximum energy density of 9.6 Wh kg^{-1} at the power density of 223 W kg^{-1} as well as good cycling stability with 78% capacitance retention after 10 000 cycles at 2 A g^{-1}. These desirable electrochemical properties of HPC/PANI composites are very promising and significant for the development of high performance supercapacitors.

2. Experimental

2.1. Materials

N,N-dimethyformamide (DMF) and anhydrous ferric chloride ($FeCl_3$) were obtianed from Sinopharm Chemical Reagent Co., Ltd. Polyacrylonitrile (PAN; M_w = 150 000) and polyvinyl-pyrrolidone (PVP; M_w = 1 300 000) were from Macklin. Hydrochlorie acid (HCl) and concentrated nitrate (HNO_3) were obtained from Beijing Chemical Works. Aniline was purchased from Xilong Chemical Works. All chemicals were used as received and without further purification. Deionized water was prepared by Water Purification System of LAB-UV-20 of Laibopate technology development Co., Ltd in Changchun.

2.2. Preparation of freestanding hierarchically porous carbon materials (HPC)

First of all, 1.5 g PAN and 1.5 g PVP was dissolved in 10 ml DMF solution. After stirring at room temperature (~25 °C) for 12 h, the precursor solution of PAN/PVP/DMF was obtained. Then, a right amount (~0.5 ml) of the precursor solution was drop on a quartz