Journal of Power Sources 319 (2016) 73–81

Contents lists available at ScienceDirect

Journal of Power Sources

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

Preparation of morphology-controllable polyaniline and polyaniline/graphene hydrogels for high performance binder-free supercapacitor electrodes

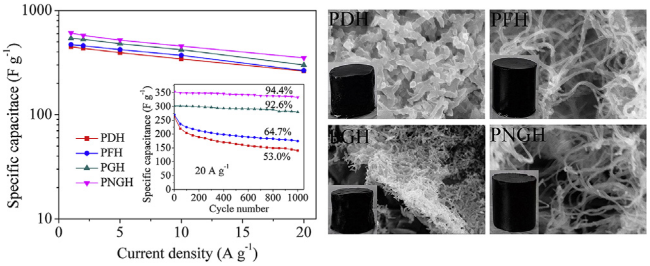
Jinwei Luo [a], Wenbin Zhong [a, *], Yubo Zou [a], Changlun Xiong [a], Wantai Yang [b]

[a] College of Materials Science and Engineering, Hunan University, Changsha 410082, China
[b] Department of Polymer Science, Beijing University of Chemical Technology, Beijing 100029, China

HIGHLIGHTS

- Polyaniline and polyaniline/graphene hydrogels are analyzed.
- Hydrogels show high specific capacitances and prominent cycling stability.
- Freeze-dried hydrogels display excellent mechanical performances.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form
16 March 2016
Accepted 1 April 2016
Available online 15 April 2016

Keywords:
Polyaniline
Graphene
Hydrogels
Mechanical strength
Supercapacitors

ABSTRACT

Polyaniline (PANI) and its composite hydrogels have been considered as a unique supercapacitor electrode material due to their three dimensional (3D) porous structures, formed conducting networks, high specific surface areas and fast electron/ion transfer. Herein, dendritic and long fibrous PANI nanostructure hydrogels (PDH and PFH), dendritic PNAI nanofiber/graphene and long PANI nanofibers/Nitrogen-doped graphene composite hydrogels (PGH and PNGH) were prepared by integration polymerization of aniline and hydrothermal process. It was found that the addition of *p*-Phenylenediamine (PPD) not only controlled the morphologies of PANI from dendritic to long fibrous, but also facilitated the graphene oxide (GO) into nitrogen-doped graphene. Furthermore, after freeze-drying, PDH and PGH exhibited a max compressive strength of 9.5 and 9.6 KPa, respectively; while the max compressive strength of PFH and PNGH constructed with long PANI nanofiber is 79.9 and 75.8 KPa, respectively. Directly using these prepared hydrogels as electrodes for supercapacitors, it was found that PDH, PFH, PGH and PNGH exhibited high specific capacitances of 448.6, 470, 540.9 and 610 F g^{-1}, respectively, at the current density of 1 A g^{-1}. It is expected that the prepared PDH, PFH, PGH and PNGH can be directly applied in the field of high performance energy storage devices.

1. Introduction

Nowadays, supercapacitors attract great attentions owing to their unique features, such as high power density, high cycle life and quick charging-discharging rates, *etc*. According to the energy-

---

* Corresponding author.
E-mail address: wbzhong@hnu.edu.cn (W. Zhong).

http://dx.doi.org/10.1016/j.jpowsour.2016.04.004

storage theory, supercapacitors can be divided into electrical double-layer capacitors (EDLC) and pseudocapacitors. The capacitance of EDLC arises from the physical electrostatics accumulation between electrode and electrolyte; while pseudocapacitance comes from the fast and reversible faradaic reaction occurred on the surface of electrode [1–4].

Polyaniline (PANI) as one of the typical conducting polymers, has been investigated extensively because of its low cost, easy synthesis, environmental stability, unique doping/de-doping property and relatively high conductivity [5–7]. Based on these advantages, PANI is reasonably considered as a good candidate for supercapacitor electrode material with expected high specific capacitance [8–11]. In the past diligence, when PANI powders were used in supercapacitor electrode, the supercapacitor usually showed a low rate capability and relatively poor cycling stability which was mainly attributed to the slow charge transfer reaction occurred in PANI, as well as the mechanical degradation caused by swelling and shrinkage of conjugated polymer chain during the charge-discharge process. In order to improve the electrochemical performance of PANI in supercapacitor, PANI hydrogel is designed and prepared because of its increased specific surface area, three-dimensional (3D) porous structure, continuous conducting framework and fast transport of charges and ions [12]. When PANI hydrogel is used in electrode, it only contains small molecule dopant and/or gelator prepared through direct polymerization of aniline, so it exhibits excellent electrochemical performance including specific capacitance, rate capability and cycle stability [13–15]. However, when PANI hydrogel is mixed with non-electroactive polymer, its electrochemical performance goes down and cannot meet application requirement; but it shows excellent mechanical strength [16,17]. Thus to develop new PANI hydrogel with better electrochemical performance and mechanical strength is still a challenge up till now.

Graphene, a two-dimensional material composed of sp^2 bonded carbon atoms, possesses many unique properties including high electrical conductivity (theoretically 10^7 S m^{-1}), specific surface area (theoretically 2630 m^2 g^{-1}) and mechanical properties, *etc.*, raises quite interest in being used as electrode materials for EDLCs since it is discovered. Furthermore, its theoretical capacitance value is up to 550 F g^{-1} with the entire utilization of the specific surface area [18,19]. However, graphene derived from graphene oxide (GO) exhibits relative low capacitance value (100–200 F g^{-1}) due to the decreased accessible specific surface area caused by their easily restacking property [20,21]. Aside from that, the process of preparing GO from natural graphite is tedious and time consuming by Hummers method [22]. In order to make full use of the excellent properties of PANI and graphene as well as overcome the disadvantages of them when be used as electrode material alone, compositing graphene and PANI into hybrid electrode materials is a possible approach to achieve high electrochemical performance because of the synergistic effects between them [23]. Generally, the chemical preparation of PANI/graphene hybrid material always involves two steps: polymerization of aniline and reducing GO, wherein GO and aniline are used as raw material. While a binder is required during the preparation of powder-based PANI/graphene composite electrode [24–28], which might affect the electrochemical performance of prepared PANI/graphene composite. On the other hand, PANI/graphene composite film can be easily made into electrode without using any binders, which is prepared by chemical oxidative polymerization of aniline in the presence of 3D porous reduced GO (rGO) or rGO paper [29–31]. Recently, 3D porous PANI/graphene hydrogel has been developed from GO/PANI nanofibers suspension through a hydrothermal co-assembly process, which then can be cut into support-free slices and used directly as electrode [32]. In this approach, PANI nanofibers shall be prepared before the hydrothermal process, while the concentration of PANI nanofibers in the suspension is constrained due to its poor dispersibility. Based on the above results, it still attracts researchers to develop a better strategy to prepare large scale graphene/PANI composite that can be directly used as binder-free electrode with high electrochemical performance.

Herein, we provide a novel strategy to prepare PANI and PANI/graphene hydrogels: (1) 3D PANI dendritic and long nanofiber hydrogels (PDH and PFH), (2) dendritic PNAI nanofiber/graphene hydrogels and (3) long PANI nanofiber/N-doped graphene hydrogels (PGH and PNGH). This strategy involves an integrated route: polymerization of aniline and then a hydrothermal process. In the present system, the additive PPD not only controls the morphology of PANI from dendritic to long nanofibrous, but also benefits the generation of nitrogen-doped graphene; while the hydrothermal process endows prepared hydrogels good mechanical properties. By this means, the prepared PDH, PFH, PGH and PNGH can be directly cut into electrodes for capacitors and offer prominent electrochemical performance.

2. Experimental section

2.1. Materials

Natural graphite (325 mesh, Qingdao Henglide Graphite Co., Ltd., China), phytic acid (PA) (50%, wt/wt in water, Sigma-Aldrich). Sodium nitrate ($NaNO_3$), sulfuric acid (98% H_2SO_4), hydrochloric acid (HCl), aniline, potassium permanganatepre ($KMnO_4$), hydrogen peroxide (30% H_2O_2), ammonium persulfate ($(NH_4)_2S_2O_8$) (APS) and *p*-phenylenediamine (PPD) were purchased from Sinopharm Chem. Reagent Co., Ltd. (Beijing, China). All commercial reagents were used directly without any further purification except the aniline monomer was distilled prior to use.

2.2. Preparation of graphene oxide (GO)

GO was prepared from natural graphite by a modified Hummers method as we described elsewhere [22,33].

2.3. Preparation of PDH, PFH, PGH and PNGH hydrogels

A typical preparation process of PNGH was described as follow: Firstly, 6.8 mL of GO (4.4 mg mL^{-1}) and 1.54 mL of phytic acid (PA) were added into a 50 mL Teflon-lined stirring at 0–5 °C. After 5 min stirring, PPD solution (30 mg PPD dissolved in 3 mL of deionized water) and 0.74 mL of aniline were dropped into the above solution. After a further 15 min stirring, APS solution (1.902 g APS was dissolved into 8 mL deionized water) was added into the mixture to initiate the polymerization of aniline. Thus the mass ratio of GO/PPD/aniline was 1:1:25, the molar ratio of (aniline and PPD)/APS was 1:1, and the molar ratio of (aniline and PPD)/PA was 5:1. The concentration of GO was 1.5 mg mL^{-1}, and the total volume of mixture was 20 mL. The stirring was stopped 5 s later, while the reaction kept running for another 1 h at 0–5 °C, and the obtained hydrogel was labeled as PNGH-1. And then the Teflon-lined containing hydrogel was sealed in a stainless steel autoclave and heated to 180 °C for 3 h. When the autoclave was naturally cooled down to room temperature, the PNGH hydrogel was obtained. Additionally, PGH hydrogel was fabricated following the same process as preparing PNGH but without adding PPD to control the morphology. PFH hydrogel was fabricated according to the same process as preparing PNGH but without adding GO. PDH hydrogel was fabricated according to the same process as preparing PGH but without adding GO. GH hydrogel was prepared with pure GO in the same way.