Journal of Power Sources 302 (2016) 92–97

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Conductive porous sponge-like ionic liquid-graphene assembly decorated with nanosized polyaniline as active electrode material for supercapacitor

K. Halab Shaeli Iessa [1], Yan Zhang [1], Guoan Zhang*, Fei Xiao, Shuai Wang

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

HIGHLIGHTS

- Self-assembly of three-dimensional porous ionic liquid–graphene nanohybrid sponge.
- Electropolymerization of polyaniline nanorods on ionic liquid–graphene substrate.
- Freestanding porous polyaniline–ionic liquid–graphene electrode for supercapacitor.

ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form
8 October 2015
Accepted 10 October 2015
Available online xxx

Keywords:
Sponge-like graphene assembly
Ionic liquid
Polyaniline nanorod
Freestanding electrode
Supercapacitor

ABSTRACT

We report the development of three-dimensional (3D) porous sponge-like ionic liquid (IL)–graphene hybrid material by integrating IL molecules and graphene nanosheets via self-assembly process. The as-obtained IL–graphene architecture possesses high surface area, efficient electron transport network and fast charge transfer kinetics owing to its highly porous structure, and unique hydrophilic properties derived from the IL anion on its surface, which endows it with high desire for supercapacitor application. Redox-active polyaniline (PANI) nanorods are further decorated on IL–graphene scaffold by electropolymerization. When utilized as freestanding 3D electrode for supercapacitor, the resultant PANI modified IL–graphene (PANI–IL–graphene) electrode exhibits a specific capacitance up to 662 F g^{-1} at the current density of 1.0 A g^{-1}, with a high capacitance retention of 73.7% as current densities increase from 1.0 to 20 A g^{-1}, and the capacitance degradation is less than 7.0% after 5000 charge–discharge cycles at 10 A g^{-1}.

1. Introduction

Recent progress in energy-related fields requires the development of high-performance energy storage devices with high power density and high energy density [1]. Nowadays, great research interest has been aroused in the innovation of electrode materials and the design of suitable electrode configuration for energy storage devices. Especially, mesoporous carbon, one of the three-dimensional (3D) porous carbon based nanomaterials, has been demonstrated to be an attractive electrode material for supercapacitors because of its excellent electrochemical performance derived from its high surface area for charge storage, and the interconnected pore structure and controlled pore size that facilitate the transport of ions and electrons, as well as the high electrical conductivity and good stability [2–4]. Furthermore, the macroscopic 3D porous graphene assemblies, such as graphene hydrogels/aerogels [5], graphene foam [6], graphene nanomesh [7,8], and some other micropores or mesopores frameworks [9], have also become the focus of considerable research during recent years for their inherited electrical, mechanical and chemical properties from their basic building block, two-dimensional (2D) graphene nanosheets, and therefore hold great promising in adsorption [5], energy conversion and storage system [6,9] and nanoelectronics [10]. Especially for supercapacitor, the 3D functional graphene materials possess multilevel porous architectures, multi-dimensional conductivity and low mass transport resistance, which are preferred from the view point of fast mass and electron transport kinetics and therefore give

---

* Corresponding author.
E-mail address: zhangguoan@gmail.com (G. Zhang).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jpowsour.2015.10.036
0378-7753/© 2015 Elsevier B.V. All rights reserved.

rise to an improved supercapacitive performance [6]. However, graphene nanosheets usually trend to restack by the strong van der Waals forces and $\pi-\pi$ interaction [11]. Meanwhile, the graphene-based material is hydrophobic in nature due to the loss of surface oxygen-containing groups after reduction by the hydrothermal process. Both of which are detrimental for their sufficient access to electrolytes. On the other hand, the electrical double-layer capacitance (EDLC) of graphene-based materials is much lower than the pseudocapacitance inherent to the redox active materials that store energy through the surface Faradic redox reaction [12].

Here we present the preparation of a new type of 3D functionalized graphene assembly, i.e., porous sponge-like ionic liquid (IL)–graphene hybrid material, and explore its application as active electrode material for high-performance supercapacitor. IL with adjusted properties by changing its anion and cation can be used to modify other nanomaterials to improve their performance [13,14]. Previous studies demonstrated that the graphene nanosheets can be functionalized with IL molecules via electrostatic and cation-π or $\pi-\pi$ interactions. The resultant all-solid-state supercapacitor based on IL functionalized graphene coated flexible indium tin oxide electrode and IL-gel polymer electrolyte exhibited high performance due to a surface charge generated from the IL cations on graphene sheet, which enables large accessible surface area wettable by IL based gel polymer electrolyte [15]. In our work, we found that IL (1-Butyl-3-methylimidazolium tetrafluoroborate, $BMIMBF_4$) molecules and graphene nanosheets can be co-assembled into 3D macroscopic sponge-like material, which is lightweight and mechanically strong, with dense interconnects porous inside. As far as we know, this is a new type of IL–graphene hybrid material that has never been reported previously. The introduction of hydrophilic $BMIMBF_4$ molecules into graphene assembly effectively prevents the restacking of graphene nanosheets. As a result, the resultant 3D IL-graphene hybrid material possesses increased surface area and faster charge transfer kinetics in comparison with pristine graphene sponge material, and unique hydrophilic properties due to the presence of IL anion, which dramatically enhance its double-layer capacitance by facilitating the contact between electrode and aqueous electrolyte, as well as the diffusion of electrolyte ion to active sites. Moreover, IL–-graphene hybrid sponge material with good mechanical stability and acceptable electronic conductivity can be directly used as freestanding electrode for supercapacitor without any binders or conducting additives, which are highly desirable for its promising application in lightweight and flexible supercapacitor devices.

The supercapacitive performance of IL–graphene sponge has further been improved by using it as a robust scaffold to immobilize polyaniline (PANI) conducting electroactive polymer in it. The combination of carbon and pseudo-capacitive nanomaterials such as metal oxides and conductive polymers has been proved to be an efficient strategy to increase the power density as well as the energy density of the nanohybrid electrode materials. Herein, the coral-like PANI nanorods are decorated on freestanding IL–-graphene electrode via electropolymerization, where a large number of IL molecules on graphene surface can provide more active site for binding PANI nanorods onto it. Owing to the synergistic combination of the unique electrical, chemical and structural properties of individual components in PANI–IL-grapehene nanocomposite, the resultant freestanding PANI–IL-grapehene electrode exhibits a specific capacitance up to 662 F g^{-1} at the current density of 1.0 A g^{-1}, with a high capacitance retention of 73.7% as current densities increase from 1.0 to 20 A g^{-1}, and the capacitance degradation is less than 7.0% after 5000 charge–discharge cycles at 10 A g^{-1}. Therefore, we envision that this work might provide a new design of nanohybrid electrode material for high-performance energy-related systems.

2. Experimental

2.1. Synthesis of porous sponge-like graphene-ionic liquid assembly

GO synthesized by modified Hummer's method was washed with distilled water and dried under vacuum [16]. Then GO powder and $BMIMBF_4$ with a ratio of 40 mg to 1.0 mL were dispersed in DMF to form a homogenous suspension after 1 h sonication, the concentration of GO in DMF was 8 mg mL^{-1}. The mixture was then sealed in Teflon-lined autoclave and maintained at 180 °C for 12 h. After naturally cooled to room-temperature and freeze-dried under vacuum, the sponge-like 3D IL–reduced GO (rGO) cylinder was obtained. The pristine rGO cylinder was fabricated under the same procedure without the addition of IL.

2.2. Electropolymerization of PANI on IL–rGO substrate

The IL–rGO cylinder was cut into pieces and used as freestanding electrode. For electropolymerization of PANI on IL–rGO electrode, IL–rGO electrode was immersed in a 1.0 M H_2SO_4 electrolyte containing 0.05 M aniline monomer at a constant potential of 0.8 V for 1 min and subsequently constant current density of 2 mA cm^{-2} for the nucleation and growth of PANI nanorods on IL–rGO electrode.

2.3. Characterization

Scanning electron microscopy (SEM) images were taken on a FESEM instrument (SIRION 200, FEI, Nederland). Fourier transform infrared (FTIR) spectra were obtained on Bruker VERTEX 70 FTIR spectrophotometer (Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed on VG ESCALAB 250 spectrometer with monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer. Nitrogen adsorption/desorption isotherms were obtained at 77 K on an accelerated surface area and porosimetry system (ASAP 2020, U.S.) using the Brunauer–Emmett–Teller (BET) method. The electrochemical characteristics were evaluated by cyclic voltammetry (CV), galvanostatic (GV) constant-current charge–discharge and electrochemical impedance spectroscopy (EIS) using a CHI 660E electrochemical workstation (Shanghai CH Instruments Co., China). A conventional three-electrode system was adopted. The working electrode was PANI–IL–rGO electrode, which was sandwiched between two Pt foil sheets to enable a strong contact at the junctions and connected to the CHI 660E electrochemical workstation. And the counter and reference electrodes were platinum plate and Ag/AgCl, respectively. On the basis of the charge/discharge curve, the specific capacitance is calculated by the equation: $Cs = i\Delta t/m\Delta E$, where i in A is the discharge current, Δt in s is the discharge time, m in g is the mass of the active electrode material, and ΔE in volts is the voltage range of discharge after IR drop [6].

3. Results and discussion

The sponge-like cylindrical IL–rGO material is shown in Fig. 1A inset, which is lightweight and mechanical strong, with highly porous structures inside (Fig. 1A and B). The high-magnification SEM image reveals that the IL–rGO sponge possesses abundant well-defined hierarchical macropores and mesopores, and the pore walls are made up of stacked graphene nanosheets (Fig. 1C and D). The specific surface area of IL–rGO sponge calculated on the basis of the BET theory is 273.6 m^2 g^{-1}, which is higher than that of pristine rGO sponge (205.8 m^2 g^{-1}), indicating that the introduction of IL molecules effectively prevents the aggregation of graphene nanosheets during the self-assembly process, hence