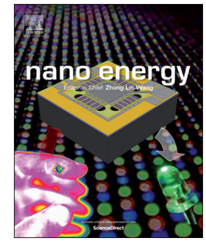
Nano Energy (▮▮▮▮) ▮, ▮▮▮-▮▮▮

Available online at www.sciencedirect.com

ScienceDirect

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



RAPID COMMUNICATION

Q2 Low cost and flexible mesh-based supercapacitors for promising large-area flexible/wearable energy storage

Chenglong Shi[a], Qing Zhao[a,b,*], Heng Li[a], Zhi-Min Liao[a,b],
Q1 Dapeng Yu[a,b,*]

[a]*State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, PR China*
[b]*Collaborative Innovation Center of Quantum Matter, Beijing, PR China*

Received 21 February 2014; received in revised form 12 March 2014; accepted 22 March 2014

KEYWORDS
Supercapacitors;
Low cost;
Flexible;
Mesh-type electrodes;
Pen-ink

Abstract
A simple, low cost and efficient flexible sandwich structure supercapacitor is developed using stainless steel mesh as electrode and commercial pen ink as active material by means of a facile and environment-friendly process. The devices show good capacitance performance, such as high specific capacitance, low inner resistance, high energy density and power density, and ultra-long cycle lifetime. The use of mesh and pen ink significantly lower the fabrication cost of supercapacitors which feature light weight and highly flexible characteristics. The stable and robust ink film on mesh electrode makes it fully compatible for conventional carbon material modification to fabricate pseudocapacitors. The comparison between the mesh-type and plate-type electrode supercapacitors certificates the good electrochemical performance of pen ink film and the advantages of mesh-type electrode. The simple dip-coating method is easily scalable for making large-scale flexible and wearable energy storage devices based on mesh and carbon ink.

Introduction

The contradiction between limited availability of fossil fuel and increasing energy requirement has become more urgent as the development of modern society. Thus, various kinds of energy harvesting devices have been invented and

Q3 *Corresponding authors at: State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, PR China. Tel./fax: +86 10 62753673.
E-mail addresses: zhaoqing@pku.edu.cn (Q. Zhao), yudp@pku.edu.cn (D. Yu).

http://dx.doi.org/10.1016/j.nanoen.2014.03.011
2211-2855/

developed, including solar cells [1], water splitting devices [2], triboelectric nanogenerators [3], and thermoelectric generators [4]. Besides energy harvesting, energy storage is very important for investigation because once energy is captured from the environment, the storage becomes necessary, not only to prevent wasting the surplus energy but also to guarantee a stable output of the converted energy in electrical system. As one of the most promising type of energy storage devices, supercapacitors or electrochemical capacitors own some unique advantages in high power density, ultra long cycle lifetime, high rates and large current density for charge/discharge, a relative wide range of operating temperatures and safety [5]. These make them promising for applications ranging from portable electronics to hybrid electric vehicles [6]. Generally, supercapacitors can be divided into two types, electrical double-layer capacitors (EDLCs) and pseudocapacitors, by different energy storage mechanism [7]. EDLCs store electrical energy by absorption of oppositely charged ions near the electrode/electrolyte interfaces, while pseudocapacitors make use of the reversible Faradaic reactions on the electrode surface.

Flexible supercapacitors have been intensely studied as flexible/wearable power sources for next generation all-in-one portable and wearable electronics [8]. Carbon fabric has been known as flexible electrodes for supercapacitors fabricated by carbon fibers through a commercial weaving method [9], however, its low capacity limits its applications [10]. Graphene based flexible supercapacitors have been developed recently. For example, high-performance and flexible graphene-based supercapacitors have been realized by laser scribing [11]. Flexible asymmetric supercapacitors are realized by using two-dimensional MnO_2 and graphene nanosheets as cathode and anode materials [12]. Hierarchical porous graphene/polyaniline composite films have been fabricated for flexible supercapacitors [13]. On the other hand, fiber electrodes have been developed for flexible supercapacitors. For example, fiber supercapacitors utilizing pen ink as active material have been developed for flexible and wearable energy storage [14]. A coaxial single fiber supercapacitor was developed using a dip coating method [15]. Along this line of thinking, metal meshes possess many advantages as conductive substrate for supercapacitors, such as high conductivity, low cost, light weight, good mechanical strength, high bending endurance, and high temperature sinterability, etc. The higher integration level of mesh makes it easier to fabricate large-area supercapacitors for industrial production compared with fiber supercapacitors [16].

In this work, we designed and manufactured a simple and efficient flexible sandwich structured mesh-based supercapacitor (MSC) that consists of two stainless steel mesh electrodes, a spacer, and an electrolyte (Fig. 1a). The electrode active material is made from commercial pen ink, which has demonstrated advantages including simple process, low cost, high flexibility and stability, and well-established industrial production compared to various kinds of carbon materials [14]. The devices show good electrochemical performance, with a specific capacitance of 107.8 F g^{-1} at a scan rate of 2 mV s^{-1}, an energy density of 10.25 Wh kg^{-1} at a current density of 0.1 mA cm^{-2}, and a power density of 11.36 kW kg^{-1} at 5 mA cm^{-2}. Besides, this mesh-based device demonstrates a stable performance during 20,000 times cyclic voltammetry (CV) under a high scan rate of 1 V s^{-1}. Moreover, the MSCs illustrate much better flexibility compared to plate-type ones, showing no distinct decrease and stable electrochemical performance after severe bending. Furthermore, a simple dip-coating method is used to form a uniform pen ink film on the mesh electrode with strong adhesion. The robust ink film makes the device fully compatible with common carbon materials modification/incorporating process, to further improve the electric conductivity and electrochemical performance of pseudocapacitors, such as MnO_2 and $Co_xNi_{1-x}DH$. Therefore, low-cost, flexible, simple-process, long-lifetime, good-performance MSCs provide a possible solution for large-area and industrial efficient flexible/wearable energy storage and management.

Experimental

Mesh electrodes and device fabrication

The mesh/plate-type stainless steel and pen ink (from Hero, Shanghai Ink Factory in China) were used in this work as purchased. Stainless steel substrates were cut into small pieces (1×2 cm^2) first and then ultrasonically cleaned in dilute hydrochloric acid, acetone, ethanol, and deionized water for 15 min, respectively. 50 nm Ni film was deposited on the whole surface of the substrates. 50 nm Au film was deposited on the upper part of the substrates about only 5 mm in width (as shown in yellow part in Fig. 1e and f) by means of mask using magnetron sputtering to protect the specific part of Ni film where is the connecting area in the following electrochemical characterization from oxidation during annealing process. A similar method of preparing the ink film on mesh electrode is used to prepare the pen ink film on the plate electrode which is coated with 50 nm Ni film and Au film using magnetron sputtering. The final working area on the electrode is 1.5×1 cm^2. The following electrochemical characterization is performed using a two-electrode system in 1 M KCl aqueous solution. An ultrasonic-assistant dip-coating method was used to prepare the required mesh/plate-type electrodes. The concrete operating procedure was as follows: the stainless steel substrates were immersed into ink solution in an ultrasonic cleaner for 1 min, taken out, annealed on the hot plate in air. The mass loading of ink film on the prepared mesh/plate electrodes is about 0.44 mg cm^{-2} and 0.2 mg cm^{-2}, respectively. Two pieces of PET in proper size and double-sided adhesive (3M Company, America) were used to pack the complete devices of mesh/plate-type electrode supercapacitors with a porous polymer spacer between the two electrodes. The thickness of the polymer spacer is 10 μm.

Pseudocapacitive materials coating

MnO_2-coating was as follows: the prepared ink based electrodes were immersed into the 0.1 M $KMnO_4$ solution at 80 °C. Then the electrodes were taken out, washed with deionized water and annealed at 300 °C in air for 0.5 h. The mass loading of MnO_2 was 0.62, 0.74, 0.97, 1.08 mg cm^{-2} for the immersing time of 0.5 h, 1 h, 2 h, and 3 h, respectively.

Please cite this article as: C. Shi, et al., Low cost and flexible mesh-based supercapacitors for promising large-area flexible/wearable energy storage, Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.03.011