Nano Energy (2015) 11, 518–525

Available online at www.sciencedirect.com

ScienceDirect

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

RAPID COMMUNICATION

Super-high rate stretchable polypyrrole-based supercapacitors with excellent cycling stability

Yan Huang[a], Jiayou Tao[b], Wenjun Meng[a], Minshen Zhu[a], Yang Huang[a], Yuqiao Fu[a], Yihua Gao[b], Chunyi Zhi[a,c,*]

[a]*Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong, China*
[b]*Wuhan National Laboratory for Optoelectronics (WNLO), and School of Physics, Huazhong University of Science and Technology (HUST), 1037 Luoyu Road, Wuhan 430074, China*
[c]*Shenzhen Research Institute, City University of Hong Kong, Shenzhen 518000, China*

Received 2 August 2014; received in revised form 14 October 2014; accepted 15 October 2014
Available online 27 November 2014

KEYWORDS
High rate;
Stretchable supercapacitors;
Polypyrrole;
Cycling stability;
Electrodeposition

Abstract
The performance and cycling stability of stretchable energy storage devices, such as supercapacitors and batteries, are limited by the structural breakdown arising from the stretch imposed and large volumetric swelling/shrinking. This work demonstrates a very facile and low-cost approach to fabricate stretchable supercapacitors with high performance and excellent cycling stability by electrochemical deposition of polypyrrole (PPy) on smartly-tailored stretchable stainless steel meshes. The fabricated solid-state supercapacitors possess a capacitance up to 170 F/g at a specific current of 0.5 A/g and it can be effectively enhanced to 214 F/g with a 20% strain. Moreover, they can be operated at a very high scan rate up to 10 V/s, which are 1–2 orders of magnitude higher than most rates for the PPy electrodes measured even in aqueous electrolytes. Even significantly, the fabricated solid-state supercapacitors under 0% and 20% strains achieve remarkable capacitance retentions of 98% and 87% at a very high specific current of 10 A/g after 10,000 cycles, respectively, which are the best for PPy-based solid-state flexible supercapacitors, to the best of our knowledge. The key factors and mechanisms to achieve such high performance are discussed. This facile and low-cost approach developed for fabricating stable and stretchable supercapacitors with high performances could pave the way for next-generation stretchable electronics.

*Corresponding author at: Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong, China. Tel.: +852 3442 7891; fax: +852 3442 0538.
E-mail address: cy.zhi@cityu.edu.hk (C. Zhi).

http://dx.doi.org/10.1016/j.nanoen.2014.10.031
2211-2855/

Introduction

Cost-effective and performance-attractive devices with long-term stability are essential for stretchable energy storage and conversion technologies, which receive considerable attention recently [1,2], for allowing many unprecedented applications possible such as future smart biosensors and clothes [3-6]. The supercapacitor in particular is one important category of energy storage devices for its high power density, fast rate of charge-discharge, long cycling life, etc. [7-17]. These features make it superior to protect against unstable energy supply situations [11,18-23]. However, several problems need to be solved when introducing the stretchability into conventionally rigid supercapacitors. First, it is much challenging to fabricate stretchable devices. Second, the performance and cycling stability of stretchable supercapacitors are limited by the non-effective solid state electrolyte and the structural breakdown resulting from the stretch applied and large volumetric swelling/shrinking during the charge/discharge process. Substantial effort has been devoted to the fabrication of stretchable devices. For example, non-coplanar buckled structures [24-26], coplanar serpentine and wavy structures [27-30], percolating nanostructured films [31], elastomers and stretchable textile substrates [32-36] have been utilized to achieve the stretchability of devices. However, on one hand, multi-step complicated fabrications are involved in these designs, which make them cost-expensive and time-consuming; on the other hand, the high performances are very difficult to be achieved with the solid state devices even the electrodes exhibit very good electrochemical activities when they are tested in the liquid electrolytes.

Regarding the structural breakdown of electrode substances under strains, it has been found that conducting polymers such as PPy can maintain or even enhance performance under stretch due to their intrinsic stretchability [36-38]. But most reported electrochemical performances of PPy-based supercapacitors such as the shape of cyclic voltammograms (CV) and galvanostatic charge-discharge curves (CD) as well as the capacitance are somewhat frustrating. As part of efforts to improve the poor cycling stability of conducting polymers [39-46], Liu et al. [47] substantially increase the cycle number from a commonly-demonstrated 1000 to a much higher value of 10,000 and achieve a remarkable capacitance retention of 85% by deposition of a thin carbonaceous shell onto the surface of PPy. However, no cycling test under stretched states was performed in the reference. Yue et al. [36] reported that under a strain of 20%, PPy coated on elastic Nylon fabrics lose 50% of capacitance after merely 500 cycles. Thus, it is crucial to develop a facile and low-cost method that can fabricate high-performance stretchable PPy supercapacitors with an excellent long-term cycling stability for their practical applications.

Here we demonstrate a facile and low-cost strategy to effectively improve the performance and cycling stability of stretchable PPy-based supercapacitors through electrochemical polymerization of purified pyrrole monomers on smartly tailored stretchable stainless steel meshes. By cutting along a certain direction, a knitted stainless steel mesh was found to become very stretchable. Then purified pyrrole monomers were electrochemically polymerized onto the mesh. The fabricated supercapacitors increase the capacitance from the initial 170 F/g at a relaxed state to 214 F/g at a 20% strain at a specific current of 0.5 A/g. Surprisingly, the solid-state supercapacitors can be operated at super-high rates up to 10 V/s, being 1-2 orders of magnitude higher than most scan rates for PPy electrodes measured even in aqueous electrolytes. More importantly, they achieve a capacitance retention of 98% under 0% strain, and 87% under a strain of 20% applied after 10,000 cycles at a very high specific current of 10 A/g. To our best knowledge, these are the best capacitance retention values reported so far for PPy-based solid-state supercapacitors.

Material and methods

PPy electrodeposition

Stretchable stainless steel meshes with a width of 0.5 cm were washed in acetone, ethanol and deionized water, and then used as substrates. Anodic electrodeposition of PPy was conducted up to 10 min at a constant current density of 0.33 mA/cm^2 in a solution of 0.1 M p-Toluenesulfonic acid, 0.3 M sodium toluenesulfate, and 0.5% pyrrole monomer (v:v) at 0 °C. Prior to electrodeposition, pyrrole was distilled in order to purify pyrrole monomers.

Fabrication of solid-state supercapacitors

Two identical as-synthesized samples were assembled together with a gel electrolyte of H_3PO_4 and PVA (electrolyte composition: 6 g H_3PO_4, 6 g PVA, and 60 ml deionized water). After gel solidification at room temperature, the solid-state supercapacitor was obtained with the electrolyte also serving as a separator.

Characterization and electrochemical measurement

Microstructures of electrodes were characterized by SEM (Philips XL30). FTIR (AVATAR 380) was used to get the spectra of the as-synthesized PPy. Cyclic voltammetry and galvanostatic charging/discharging measurements were performed on an electrochemical station (CHI 760E). Electrochemical impedance spectroscopy was measured at frequencies ranging from 0.01 Hz to 100,000 Hz with potential amplitude of 5 mV. Supercapacitors were mounted into two clips, and stretched horizontally by a test bench (AMH-500, Yiding Co.).

Results and discussion

It is noticed that the stainless steel mesh possesses the same weaving structure as conventional textiles but electrically conductive. Although the mesh woven by a plain weave technique is not stretchable along directions of the weft and the warp, it can be stretched up to a strain of 40% along a direction of 45° to the weft or the warp, as schematically shown in Fig. 1a and b. By cutting along the dashed black lines in Fig. 1, the as-cut mesh is stretchable biaxially. This provides a facile and low-cost method to fabricate stretchable devices without resorting complicated treatments to obtain conductive and stretchable substrates. As conducting polymers such as PPy possesses the best deformability among various