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Temperature effects on electrochemical performance of carbon nanotube film based flexible all-solid-state supercapacitors

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ABSTRACT

The growing demand on flexible all-solid-state supercapacitors has accelerated the need for fundamental understanding of their response to extreme thermal environment. In this study, supercapacitors based on freestanding films composed of randomly oriented carbon nanotubes and H_2SO_4-PVA gel electrolyte were fabricated. The effect of temperature on their electrochemical behaviors was systematically investigated by using cyclic voltammogram, impedance spectroscopy and galvanostatic charge-discharge measurements at temperatures between −5 °C and 55 °C. The results indicated that the capacitance of the supercapacitor was enhanced by the increase of operating temperature while the internal resistance was reduced by virtue of the acceleration of transportation/adsorption of electrolyte ions and surface modification of the electrode. For instance, when charged with the current density of 0.2 mA cm^{-2}, the capacitance increased by 24.3% from −5 °C to 25 °C, and by 32.6% from 25 °C to 55 °C. Operating temperatures at or below 25 °C were found to facilitate the charge-discharge reversibility and long-term cycle stability. It has also been concluded that supercapacitors based on H_2SO_4-PVA gel electrolyte were not suitable for long term use at temperatures higher than 40 °C due to the aging of electrolyte.

1. Introduction

With rapidly growing demands for clean energy and flexible electronics, such as roll-up displays, hand-held portable devices, and sensor networks, supercapacitors have recently attracted increasing attention owing to their advantages of fast charge-discharge rate, long cycle life, and high power density [1–3]. As compared to supercapacitors using aqueous, organic or ionic liquid electrolyte, all-solid-state supercapacitors are particularly desirable for portable and wearable electronics because of their high flexibility, compact size, lightweight, and environmentally friendliness [4–7]. H_2SO_4/H_3PO_4/KOH-doped poly (vinyl alcohol) (PVA) gel [8–11], H_3PO_4-doped poly (2, 5-benzimidazole) (ABPBI) [12,13], potassium polyacrylate (PAAK)/KCl [7,14], and poly(ionic liquid) (PIL) [15] have been used as the solid-state electrolytes for achieving reduced leakage, improved safety and better packaging capability over their liquid counterparts. More recently, stretchable all-solid-state supercapacitors with self-healing function [16] have been fabricated by using vinyl hybrid silica nanoparticles-crosslinked polyacrylic acid electrolyte. In addition to activated carbon [17] and reduced graphene [18], carbon nanotubes (CNTs) have been frequently employed as the electrode material of flexible all-solid-state supercapacitors due to the high surface area, and excellent mechanical and electrochemical properties [19]. Some examples include CNT-coated cotton paper-shaped electrodes [20], CNT fiber/wire-shaped electrodes [21–24], and CNT film-based electrodes [25,26].

The electrochemical performance of supercapacitors is quite dependent on the working temperature [27], particularly under extreme cold or hot environment. Therefore, fundamental understanding of how temperature affects the capacitance and cycle life is of vital significance for many applications. Over the past few years, studies on temperature effects have mainly focused on non-solid-state supercapacitors. For example, Masarapu et al. [28]

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explored the electrode/electrolyte interface properties with respect to temperature changes (25–100 °C) in the supercapacitor based on organic electrolyte and single-walled CNT electrode. In nearly the same temperature range, Li et al. [27] reported the study on the temperature-dependent electrochemical behavior of an untrafine MnO_2 nanobelt supercapacitor. However, limited efforts were devoted to thermal effect of all-solid-state supercapacitors. Yuan et al. [29] investigated the effect of temperature on the electrochemical performance of a hybrid supercapacitor based on NiO and activated carbon with PVA-KOH-H_2O electrolyte between −20 and 40 °C. Hastak et al. [13] investigated the temperature dependence of the capacitance and resistance of a supercapacitor using phosphoric acid-doped ABPBI as the electrolyte and multi-walled CNT (MWCNT) powder-ABPBI-polytetrafluoroethylene (PTFE) complex-coated carbon paper as the electrode. Overall, there has been no report to date on the effect of temperature on electrochemical performance of flexible CNT film-based all-solid-state supercapacitors.

Here, we report the temperature effect of supercapacitors assembled with H_2SO_4-PVA gel electrolyte and freestanding film electrodes composed of randomly oriented MWCNTs, in the range of −5–55 °C. Cyclic voltammogram and impedance spectroscopy were applied to analyze the supercapacitor electrochemical behaviors at both low and high temperatures for comparison with those at ambient temperature. The temperature-dependent long-term cycle stability was examined using galvanostatic charge-discharge tests.

2. Experimental

2.1. Materials

The freestanding films consisted of randomly oriented MWCNTs (thickness = 2 μm and density = 807 mg cm^{-3}) were prepared at the Suzhou Institute of Nano-Tech and Nano-Bionics using the floating catalyst chemical vapor deposition (FCCVD) technique [30]. PVA powder (weight-average molecular weight, $\overline{M_w}$ = 89,000 ~ 98,000), and two-component polydimethylsiloxane (PDMS) (Sylgard® 184) were purchased from Sigma Aldrich Company. Concentrated H_2SO_4 (98%) were bought from Fisher Scientific Company. All materials were used without further treatment.

2.2. Fabrication

2.2.1. Fabrication of gel electrolyte

To obtain the H_2SO_4-PVA gel electrolyte, concentrated H_2SO_4 (2 g), PVA powder (2 g) and deionized water (20 ml) were mixed and vigorously stirred at 85 °C until the mixture solution became transparent.

2.2.2. Preparation of PDMS film

The polydimethylsiloxane (PDMS) film with the thickness of ~0.2 mm was prepared by blending the two silicone components (base and curing agent, Sigma Aldrich, Sylgard® 184) with the mass ratio of 10: 1, and then casting into a Petri dish, followed by degassing at ambient temperature for 20 min and subsequent curing at 60 °C for 3 hours.

2.2.3. Fabrication of flexible all-solid-state supercapacitor

To fabricate the CNT film electrode-based supercapacitor, the CNT film (7 mm in width) was first attached on a strip of PDMS film, followed by coating the liquid PVA-H_2SO_4 gel electrolyte onto the upper surface of the electrode. After the gel electrolyte became solid, two PDMS-CNT-electrolyte sheets were combined with another thin gel electrolyte layer in between to form a sandwiched supercapacitor as shown in the dotted region of Fig. 1.

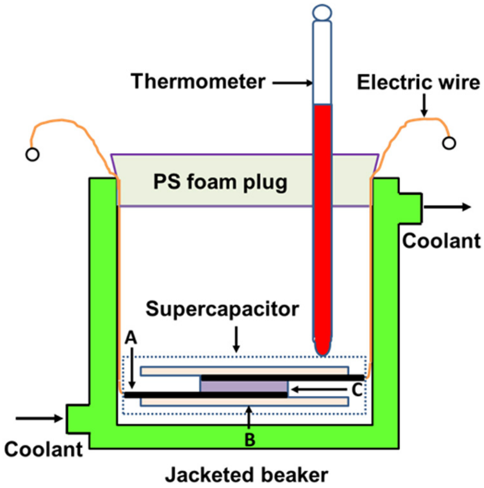

Fig. 1. Schematic of the supercapacitor and experimental setup for temperature control. In the supercapacitor profile, A, B and C refer to the CNT film-based electrode, PDMS substrate, and PVA-H_2SO_4 gel electrolyte, respectively.

2.2.4. Temperature Control

The constant experimental temperature was achieved in a self-made "mini-oven" which includes three parts: a 250 ml jacketed reaction beaker equipped with a 4 cm-thick polystyrene (PS) foam lid, a digital refrigerated circulating water bath (HAAKE K 10) and a common thermal meter (Fig. 1). The circulating water was pumped into the jacket of the beaker, and subsequently flowed back to the water bath. During the circulation, the internal air of the beaker was heated or cooled until its temperature reached to as high as that of the circulating bath. By using the circulating water bath, the internal temperature of the jacketed reaction beaker can be controlled with an accuracy of 0.02 °C. To protect the water from freezing under zero degree, 1 L commercial Zerex original green coolant was added to the circulating water. Prior to each electrochemical measurement at a certain temperature, the supercapacitor sample were laid down in the jacketed beaker for at least 30 min to equilibrate and keep the sample's temperature constant.

2.3. Characterization

2.3.1. Structure characterization of the electrode material

The surface morphology of the CNT film was examined using an Auriga 60 scanning electron microscope (SEM) at an accelerating voltage of 3.0 kV. The transmission electron microscopy (TEM) observation was conducted on a Talos F200C microscope.

2.3.2. Electrochemical Performance Characterization

Cyclic voltammogram (CV) tests were performed using a multichannel potentiostat (VMP2, Princeton Applied Research) in the potential range of 0–0.8 V with scanning rates of 20, 50, 100, 200, 500, 1000, and 2000 mV s^{-1}. The operating temperatures were between −5 and 55 °C with an incremental step of 15 °C. The electrochemical impedance spectra (EIS) at different temperatures were recorded in the frequency range from 100 kHz to 10 mHz. The galvanostatic charge-discharge cycling experiments were conducted using an Arbin battery testing system in the potential range of 0 V–0.8 V. The self-discharge processes were monitored at