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Electrospun polymer electrolyte nanocomposites for solid-state energy storage

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ABSTRACT

We report solid-state fabric supercapacitors with polymer electrolyte composites (PEC). The fabric supercapacitors were comprised of a fiber-shape PEC and electrodes. The PEC was formulated by mixing a network-forming polymer, poly(vinylidene fluoride-*co*-hexafluoropropylene) and a room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. By using a simple electrospinning technique, we could successfully fabricate a free-standing fiber-shape PEC. The electrospun PEC showed high ionic conductivity of 0.48 mS/cm and mechanical strength of 2.4 MPa. The electrodes were produced by two-step processes consisting of electrospinning and spray coating. By using these spun electrolyte composites and electrodes, fabric supercapacitors with a sandwich structure were fabricated. The resulting device exhibited typical capacitive energy storage characteristics and the measured specific capacitance was 6.72 mF/cm^2. Moreover, the device maintains its structure and electrochemical performance under repeated bending stress. This work can offer a new option for developing solid-state energy storage devices for smart textile and wearable electronic applications.

1. Introduction

Smart textiles (also known as E-textiles) that sense and respond to environmental stimuli have gained significant attention in recent years owing to their potential applications in ubiquitous healthcare, wearable electronics, and smart cloths [1–3]. For realizing such textile-based smart systems, the development of flexible and lightweight solid-state energy storage devices that can power those devices is urgently required. Among various types of energy storage devices, supercapacitor is an attractive candidate owing to its high power density, high rate capability, reliable cycling stability, and operating safety [4–6]. However, researches in the supercapacitor field typically focus on developing porous electrodes with high surface areas to maximize the energy density and the development of textile-based capacitors is still in the early stage. Thus, to successfully realize supercapacitors for an energy supply device in smart textile electronics, it is imperative to develop main components (e.g., electrode, electrolyte, and supporting substrate) and the device platform, which can be applicable to textile applications.

In general, two strategies have been used to fabricate supercapacitors for smart textiles. (i) The first strategy is to construct supercapacitor on planar cellulose paper or cotton cloth [7–9]. These materials are good substrate candidates for solid-state supercapacitors, as they are not only flexible but also can be readily integrated with functional materials such as graphene, carbon nanotube, metal oxide, and liquid/solid electrolyte. The device with cotton cloth and graphene sheet showed a high specific capacitance (C_{sp}) of 81.7 F/g [7]. All the solid-state flexible supercapacitors with bacterial nanocellulose papers exhibited a C_{sp} of 20 mF/cm^2 [8]. However, employing these devices into smart textile has been restricted because they consist of liquid electrolyte or a 2D solid electrolyte film. (ii) The second strategy is directly fabricating 1D fibrous supercapacitors and weaving them to form the fabric structure [10–12]. Fiber structured supercapacitors made of carbon nanotube yarn, graphene, and carbon nanotube powder have recently been reported. Coaxial fiber supercapacitor using all-carbon material electrodes showed a capacitance value of 86.8 mF/cm^2 and excellent cycling performance [10]. Qu et al. reported graphene-

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based fibriform supercapacitors with a C_{sp} of 1.7 mF/cm^2 [11]. Nevertheless, such 1D-structured fibriform device still suffers from complicated fabrication processes, complex structures, and low mechanical flexibility. Therefore, developing easy-to-forming 1D fiber-shape electrodes and electrolyte materials is critical to provide a simple yet versatile fabrication route for flexible fabric supercapacitors. Polymer electrolyte composites (PECs) based on ionic liquids (ILs), known as ion gels, have attracted considerable research interest as nonvolatile electrolytes for energy storage applications [13–15]. Ion gel consists of a room temperature IL gelled by a polymer matrix that is swollen at the IL of interest. By optimizing the chemistry and composition of the component materials, a PEC with high ionic conductivity (> 1 mS/cm) and sufficient mechanical strength (> 1 MPa) can be prepared. Thus, various types of PEC materials based on IL including bulk composites, films, and micro patterns have been formed for electronic and energy devices [16–18]. However, fiber shape PEC material containing IL as a major component (ca. 80 wt%) applicable to smart textile has not been demonstrated.

Herein, we developed a facile method to fabricate a supercapacitor consisting of electrospun PEC microfiber and free-standing microfiber electrodes constructed by electrospinning technique. The PEC fibers can be easily fabricated using a simple electrospinning technique without complicated, multi-step processes required for general textile devices. The PEC solution was formulated by blending a network forming polymer, poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-HFP)) and an IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]). P(VDF-HFP) was chosen here because of its high mechanical strength and good compatibility to the IL. [EMIM][TFSI] was employed due to its high ionic conductivity and wide electrochemical window (> 4 V). These materials were dissolved in dimethylformamide (DMF)-acetone co-solvents. During the electrospinning process, a fiber-shape PEC was formed by the phase-separation of crystalline domains of the host polymer in the [EMIM][TFSI]. The resulting free-standing electrospun PEC fibers exhibited both high ionic conductivity (0.48 mS/cm) and good mechanical strength (2.4 MPa). To obtain free-standing electrodes, sequential fabrication of electrospun structuring polymer mat, followed by spray coating of conducting polymer, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been successfully employed. Using these spun electrodes and electrolytes, solid-state supercapacitors with a sandwich structure ((P(VDF-HFP))/Ag nanowire (NW)/PEDOT:PSS electrode/PEC fibers/PEDOT:PSS/Ag NW/P(VDF-HFP) electrode) were successfully demonstrated. The resulting fabric devices showed a C_{sp} of 6.72 ± 0.8 mF/cm^2 at a scan rate of 100 mV/s with good cycling stability and 82.6% specific capacitance retention after 1000 charging and discharging cycles. The device also exhibited a capacitance retention of 71% after 100 repeated mechanical bending cycles with a bending radius of 6 cm. To the best of our knowledge, this is the first report of electrospun PEC with high IL concentration (~80 wt%) and the application of these electrolyte fibers to solid-state fabric supercapacitors using high throughput solution processes. We believe that the combination of the PEC microfiber and fiber-shaped polymer electrodes can offer a new option for developing solid-state energy storage devices for smart textile applications.

2. Experimental methods

2.1. Materials

The materials were as follows: P(VDF-HFP) with M_n = 130,000 g mol^{-1}, Sigma-Aldrich; [EMIM][TFSI], EMD Chemicals; Ag NW solution, Nanopyxis; PEDOT:PSS (aqueous dispersion), Heraeus (Clevios PH 1000).

2.2. Preparation of the PEC solution

The PEC solution was prepared by co-dissolving P(VDF-HFP) and [EMIM][TFSI] in co-solvent of acetone and DMF (volume ratio of acetone:DMF = 1:4). The weight ratio between the polymer and IL was kept at 1:4. The solution was stirred at room temperature for 6 h.

2.3. Fabrication of fabric supercapacitors

Free-standing P(VDF-HFP) microfibers mat was produced by the electrospinning method. Electrospinning setup itself consists of a solution container, a syringe pump, a grounded collector, and a high voltage power supply. Glass substrate was placed on the collector plate to act as the receiver. To prepare P(VDF-HFP) fibers, electrospinning was conducted at 15 kV, and the feed rate of the solution was 3 mL/h. The collection time to produce a 50 μm-thick P(VDF-HFP) fiber mat with a 15 × 15 cm^2 area was ~40 min. The P(VDF-HFP) fibers mat was peeled-off from the glass substrate using a tweezer. Then, 3 mL-Ag NW and 3 mL-PEDOT:PSS solutions were sequentially spray coated onto the polymer fibers. Electrospun PEC microfibers was then deposited on the sample. For PEC, electrospinning was performed at 18 kV with a solution feed rate of 2 mL/h. The distance between the needle and the collector was 20 cm for all the experiments. Finally, the fabric supercapacitor was fabricated by assembling another P(VDF-HFP)/Ag NW/PEDOT:PSS electrode.

2.4. Characterization and measurement

The microstructure of the PEC samples was investigated by X-ray diffraction (XRD) using a DMAX-2500 (Rigaku) X-ray diffractometer. Scanning electron microscopy (SEM) observations were conducted using a FEI Phenom microscope. Thermogravimetric analysis (TGA) data were obtained using a TGA Q50 (TA Instrument). Tensile tests were performed using an Instron 5569 universal testing machine. The chemical bonding states of the PEC was analyzed using a synchrotron radiation photoelectron spectroscopy (SRPES) in Pohang Acceleration Laboratory (PAL, 4D beamline). A potentiostat (VERSASTAT4, Princeton applied research) was used to measure the electrochemical properties of the supercapacitors.

3. Results and discussion

3.1. Fabrication of PEC and fabric supercapacitor

The schematic fabrication process of the fabric supercapacitor is described in Fig. 1a. First, a free-standing P(VDF-HFP) micro filaceous mat was prepared on glass substrates by the electrospinning method (Fig. 1b). Electrospinning provides a remarkably simple and effective way for generating polymer fibers with diameters down to a few tens of nanometers [19]. To supply electrical conductivity to the P(VDF-HFP) microfibers, a Ag NW was directly spray-coated on the top of the sample. The goal of this work is to realize fabric energy storage devices based on a simple solution process. Additionally, the electrospun electrolyte fibers are so soft that physical vapor deposition of a metal electrode on the PEC was difficult. Ag NWs and their composites have been used into supercapacitors as a conductive electrode. These electrodes exhibit high electrical conductivity (> 100 S/cm) and the devices showed good energy storage performance and mechanical flexibility [20,21]. Thus, we employed spray-coated Ag NWs as a charge collector of the device [22–24]. The Ag NWs are 50–100 μm in length and 50–80 nm in diameter. The average thickness of the spray coated film is about 250 nm. The average sheet resistance of the Ag NW coated sample was ~37 Ω/sq. Subsequently, conducting polymer, PEDOT:PSS was spray coated onto the pre-deposited Ag NW surface to supplement the electrochemical charge storage. The P(VDF-HFP)/Ag NW/PEDOT:PSS hybrid composite plays the roles of both electrodes and charge