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A singular flexible cathode for room temperature sodium/sulfur battery

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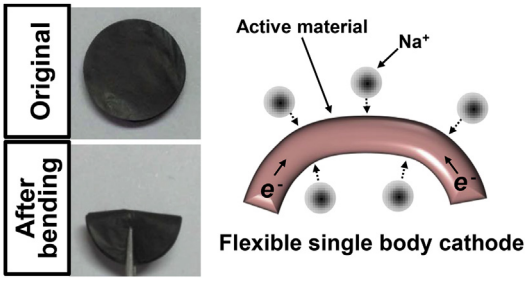
HIGHLIGHTS

- A flexible sulfurized polyacrylonitrile cathode was prepared by simple pyrolysis.
- The SPAN cathode shows rollability, and bendability to 180° without fracture.
- The cathode contains no binder, current collector and conducting additives.
- Na/SPAN cell shows good cycle performance.
- The 1st capacity of 342 mAh $g^{-1}_{electrode}$ remains 266 mAh g^{-1} after 200 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

This study introduces a new flexible cathode that contains no binder, conductive additive and current collector, but instead consists solely of a sulfurized polyacrylonitrile nanofiber (SPAN) web which is prepared by a simple pyrolysis process with low cost raw materials. This not only exhibits good electrochemical properties, but also a high flexibility, rollability, and bendability to 180° without fracture. Its feasibility as a cathode for a low cost and flexible Na/S battery is subsequently evaluated on the basis that S, PAN, and Na are cheap materials. The SPAN web delivers a high first discharge capacity of 604 mAh g^{-1} – electrode (1473 mAh g^{-1} – sulfur) at 0.01 C based on sulfur content. In cycle performance at 0.1 C, a first discharge capacity of 342 mAh g^{-1} – electrode is obtained and remains over 266 mAh g^{-1} – electrode after 200 cycles along with the coulombic efficiency near 100% from the second cycle. In terms of rate capability, it is shown to be capable of delivering a capacity of as high as 71 mAh g^{-1} at 1 C. The reversible electrochemical reaction of the SPAN web with Na is related to a reversible bond between the C–S and S–S bonds of the SPAN web.

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1. Introduction

We currently live in a world where portable electronic devices such as cellular phones and laptop computers are much thinner and lighter than the heavy, thick, rigid, and bulky designs of the past. The future development of such devices will be therefore toward even more portable, ultrathin/lightweight, and flexible devices. Products from the developments may include roll-up displays, conformable active RFID tags, e-skins, wearable sensors, and implantable medical devices [1–7].

As such products have typically obtained their electric power from lithium ion batteries, the same goals also apply to battery technology. Consequently, there have been a number of studies aimed at developing flexible electrodes for lithium ion cells [8].

However the very limited resources of lithium (typically in the order of 20 mg kg^{-1} in the earth's crust and 0.18 mg L^{-1} in seawater) has created a high price for the metal that is expected to only increase in the future. In contrast, sodium is abundant and cheap, with concentrations as high as 28,400 mg kg^{-1} earth's crust and 11,000 mg L^{-1} in seawater. And sulfur as the cathode active material has many advantages such as high theoretical capacity of 1672 mAh g^{-1}, and abundance (340 mg kg^{-1} earth's crust). The overall electrochemical reaction of the room temperature Na/S battery is $2Na + S \rightarrow Na_2S$, along with the high theoretical energy density of 1230 W h kg^{-1}. After the first report in 2006 [9], a number of studies has been reported [10–17]. And they has pointed out overcoming the low electric conductivity of elemental sulfur and the dissolution of the high order sodium polysulfides causing the various drawbacks such as fast capacity decrease during cycling, which are similar technical hurdles found in Li–S battery, to realize the high performance Na/S battery. Although a cheap and flexible battery can contributes to commercialization of a lot of flexible electronic devices, there was no study into the possibility of flexible Na/S cells operating at room temperature [13].

Since most active materials are rigid, previous studies have tended to focus on combining them with flexible current collectors (or conducting agents) made from carbon materials or conductive paper, polymer, etc. [8,18]. This has meant that the preparation methods usually consist of two steps: the preparation of a flexible current collector, followed by its combination with a rigid active material [8]. Various methods have been used for this, such as hydrothermal reaction [19], photothermal reduction [20], pulsed laser deposition [21], ultrasonication and co-deposition [22], casting and drying [23].

Unfortunately, all of these methods bear fundamental and inevitable limitations. The foremost among these is the need for a flexible current collector that has both good flexibility and high electrical conductivity. Secondly, the flexible current collector reduces the capacity of the electrode due to its weight. Another limitation is the detachment of the active materials from the current collector by a severe physical deformation or the electrochemical reactions. Furthermore, a secondary step to attach the active material requires complex process and additional cost. Therefore, there is a strong need for a new approach to the flexible cathode which consists of only active material without a separate current collector. This concept offers many advantages in terms of simplifying the preparation process, eliminating the detachment of active material, and, most importantly, increasing the total electrode capacity. The realization of a single-body flexible cathode has, however, been delayed by the difficulties associated with achieving the right combination of high flexibility, good electrical conductivity, and good electrochemical reactivity.

Sulfurized polyacrylonitrile is well known as a cheap and high capacity cathode material suitable for lithium and sodium rechargeable cells [24–26]. During heat treatment, polyacrylonitrile forms a heterocyclic ring that provides a high electrical conductivity of 10^{-4} S cm^{-1} [26]. Thus it can be possibly used as an electrode without current collector. In addition the electrochemical properties can be further improved by varying its morphology to nanonets or nanofibers [27,28].

It is well known that a rigid material can be flexible without fracture when it has a specific nanometer scale structure: Carbon can be flexible in the forms of carbon nanotube and nanofiber [29]. Thus, in this study, SPAN webs were fabricated through the simple heat treatment with the sulfur of electrospun PAN nanofiber webs. This experiment aimed at producing a flexible cathode without a binder, conducting agent, and current collector. The electrochemical properties of the flexible SPAN cathode vs Na/Na^+ are investigated. In addition, the charge/discharge mechanism is clarified using a singular cathode.

2. Experimental

2.1. Preparation of SPAN webs

The SPAN webs were prepared by a two-step process of electrospinning PAN nanofiber webs and their pyrolysis with sulfur. An electrospinning solution was prepared by dissolving PAN (10 wt%, Mw = 150,000, Polyscience, USA) in *N*,*N*-dimethylformamide (DMF, DAEJUNG, Korea) and homogeneously dispersing it by stirring at 60 °C for 12 h. This solution (4 mL) was then loaded into a 10 mL syringe fitted with a 21-gauge metallic needle (ID: 0.51 mm, OD: 0.81 mm) at its end. A flow rate of 1.8 mL h^{-1} and high voltage of 19 kV was then applied to the needle, with the PAN nanofibers being then collected on a rotating drum (180 rpm) positioned about 18 cm from the needle tip. The as-spun PAN nanofiber web (PAN web) was then removed from the drum collector and set in an alumina boat. Afterward it was homogeneously covered with sulfur powder (Aldrich). The alumina boat was then transferred into a quartz tube furnace and pyrolyzed at 450 °C for 6 h at a heating rate of 10 °C min^{-1} under an Ar atmosphere (100 sccm flow rate). Following this, the SPAN web was analyzed by a micro element analyzer (Flash 2000 CHNS/O Analyzer, Thermo scientific, USA) (see Supporting Information, Table S1), and then punched to form a 1 cm-diameter disc that was used directly as a cathode and has a weight from 0.73 mg with a thickness of ca. 30 μm. For comparative purposes, a HT-PAN web was also obtained by pyrolyzing the PAN web under the same conditions, but without the addition of sulfur.

2.2. Electrochemical characterization

A sodium metal disc (Aldrich, 99%) and 1 M of $NaPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 = *v*/*v*, Soulbrain, Korea) were used as the anode and the electrolyte, respectively. A glass fiber filter (GF/D, Whatman, UK) was used as a separator. A SPAN web was used as a cathode without conducting agent, binder and current collector. Assembly of the Na/SPAN cell was carried out by sequentially stacking the sodium anode, glass fiber filter separator, and SPAN web. Swagelok-type cell containers were used for this, and all stages of assembly were conducted in an argon-filled glove box.

Electrochemical characterization was performed through galvanostatic tests carried out at room temperature using a WBCS3000 battery cycler (WonATech Co., Korea). A voltage range between 0.7 and 2.8 V vs. Na/Na^+ was selected, and the current densities of 0.01, 0.1, 0.5 and 1 C rates were selected based on the sulfur content of the SPAN web samples. Potentiostatic testing was conducted by means of a frequency response analyzer (VMP3, Biologic, France) operating at a scan rate of 0.1 mV s^{-1} and at room temperature.