



## Short communication

## Graphene-coated plastic film as current collector for lithium/sulfur batteries



Li Wang<sup>a</sup>, Xiangming He<sup>a,b,\*</sup>, Jianjun Li<sup>a</sup>, Jian Gao<sup>a</sup>, Mou Fang<sup>a</sup>, Guangyu Tian<sup>b</sup>, Jianlong Wang<sup>a</sup>, Shoushan Fan<sup>c</sup>

<sup>a</sup>Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

<sup>b</sup>State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China

<sup>c</sup>Department of Physics, Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, PR China

## H I G H L I G H T S

- ▶ A metal free cathode of sulfurized polyacrylonitrile is attempted.
- ▶ Using graphene coated polyethylene terephthalate film as current collector.
- ▶ 110 mAh prototype lithium sulfur cells are assembled with energy density of 452 Wh kg<sup>-1</sup>.
- ▶ The capacity retention is 96.8% after 30 cycles at 100% depth of discharge.
- ▶ The self-discharge is less than 1% after 30 days of storage at room temperature.

## A R T I C L E I N F O

## Article history:

Received 3 October 2012

Received in revised form

29 January 2013

Accepted 1 February 2013

Available online 15 February 2013

## Keywords:

Sulfurized polyacrylonitrile

Self-discharge

Current collector

Graphene

Polyethylene terephthalate

## A B S T R A C T

A metal-free battery is of great practical significance in terms of high energy density, low cost, high safety, eco-friendly and sustainability. Here a metal-free cathode, using graphene-coated polyethylene terephthalate (G-PET) film (Commercial-Off-The-Shelf) as current collector and sulfurized polyacrylonitrile (SPAN) as active material, is aiming at low cost and high energy density battery. 110 mAh prototype lithium sulfur cells are assembled using SPAN/G-PET cathode, showing energy density of 452 Wh kg<sup>-1</sup> excluding the weight of package and capacity retention of 96.8% after 30 cycles at 100% depth of discharge. The self-discharge characteristics of prototype cells are tested. After 30 days of storage at room temperature, the discharge capacity has decreased less than 1%, indicative of low self-discharge of the SPAN-based Li/S batteries. This paper shows that G-PET can be a potential promising current collector for lithium ion batteries.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Safe, low-cost, high-energy-density and long-lasting rechargeable batteries are in high demand to address environmental and energy needs for energy storage systems that can be coupled to renewable sources [1,2]. Due to their large specific capacity, abundant resources and low cost [3,4], the sulfur-based cathode materials are of great potential for the next generation of high performance lithium batteries. However, lithium/sulfur (Li/S) cells

in liquid electrolytes suffer from critical drawbacks in terms of cycling life, rate capability, and sulfur utilization. It is reported that the sulfurized polyacrylonitrile composite (SPAN) cathode material, which is structurally highly dispersed nano-sulfur embedded in a conductive matrix, shows novel performances compared to conventional elemental sulfur-based cathode by avoiding shuttle effect that is the main drawback of conventional elemental sulfur composite [5–12]. Afterward, the cycling characteristics and rate capability of SPAN cathode material are investigated for rechargeable lithium batteries [13]. Furthermore, the charge/discharge characteristics with different voltage windows, kinetics of SPAN materials, expansion and shrinkage of SPAN electrode, the electrochemical characteristics of SPAN cathode on different charge/discharge manner, the compaction strength of the electrode and safety of overcharge of SPAN cathode in rechargeable lithium

\* Corresponding author. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 89796073; fax: +86 10 89796031.

E-mail addresses: [hexm@tsinghua.edu.cn](mailto:hexm@tsinghua.edu.cn), [hexiangming@tsinghua.org.cn](mailto:hexiangming@tsinghua.org.cn) (X. He).

batteries are further studied [14–18], and the electrolyte effect on the performance of SPAN is investigated as well [19]. A rechargeable cell system with an electrochemically prelithiated SPAN as cathode and graphite as anode is studied to address the safety concerns of metallic Li negative electrodes [17,18]. The previous investigations have shown promising of SPAN for high capacity cathode with good reversibility in high capacity rechargeable batteries. Self-discharge behavior is one of the important factors for commercialization of lithium batteries [20–22], but there has been no reports of the self-discharge of SPAN cathode based Li–S cells.

In addition, current collector may be considered as inactive material and reduces the gravimetric and volumetric energy densities of the battery. Current collectors, typically aluminum foil and copper foil, account for about 15–20% by weight and 10–15% by cost of a battery [23]. Therefore, thinner, lighter foils would be preferred. However, due to easy creasing and tearing, thinner foils tend to be more expensive according to the method of preparation and harder to work with. It is clear that the current collectors must be electrochemically stable in contact with the cell components over the operating potential window of the electrode. In practice, continued corrosion of the current collectors will lead to a gradual increase in the internal resistance of the battery, with corresponding loss of the apparent capacity, at a given rate [24]. Not only that, oxidation of metal current collectors may be one of the greatest exothermic reactions in thermal runaway. Accordingly, current collector is crucially important for cost, weight and performance of batteries.

In this study, graphene-coated plastic film (Commercial-Off-The-Shelf) is attempted to be used as current collector for SPAN batteries due to its low cost and low weight. The self-discharge characteristics of SPAN electrode in rechargeable lithium batteries using graphene-coated PET film as current collectors are investigated particularly.

## 2. Experimental

Graphene-coated polyethylene terephthalate (G-PET) film is prepared as follows. PET (108N type, Hangzhou Dahua Plastics Industry Co., Ltd, China) is purchased from market. The thickness of the film is 12  $\mu\text{m}$ . Graphene (SS-1) is provided by Ningbo Smallsheet Company, China. The graphene slurry with solid content of 0.25 wt.% is prepared using DMF (*N,N*-dimethylformamide) as dispersing agent, and cast on the PET film using a scalpel, successively dried at 80  $^{\circ}\text{C}$  for 8 h before further processing.

SPAN is prepared as reported [3,7]. The sulfur content is optimized to be 42% [3]. SPAN is thoroughly mixed with acetylene black and PVdF (polyvinylidene difluoride) binder (Kynar<sup>®</sup> 761), using DMF as solvent. The weight ratio of SPAN, acetylene black and PVdF in the final dry cathode was 7:2:1. The resulting slurry is cast on G-PET film using a scalpel. The electrode is then obtained. The mass loading of active material of the resulting electrodes is around

5  $\text{mg cm}^{-2}$ . The electrodes are then dried at 120  $^{\circ}\text{C}$  under vacuum for 24 h. The plastic packaged cells are assembled in a glove box (M. Braun GmbH, Germany) with  $\text{H}_2\text{O}$  and  $\text{O}_2$  content below 1 ppm. Lithium foil is used as anode and Celgard 2400 microporous film is used as separator. The electrolyte is 1.0 M  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v). The cells are assembled by stack process with laminated soft package. The charge and discharge performance of the cells is tested at 30  $^{\circ}\text{C}$ . The normal charge procedure is composed of a constant-current of 5.0 mA up to 3.0 V. The normal discharge procedure is composed of a constant-current of 5.0 mA until the voltage dropped to 1.0 V. The cell is rested for 1 h before it begins to be discharged. The formation process, cycling 3 times at 2 mA current, is done before the cycling performance is tested.

The self-discharge rate test is carried out as follows. A cell after formation is charged to 3.0 V, and then stored at 30  $^{\circ}\text{C}$ . After a designed period, it is discharged to 1.0 V.

## 3. Results and discussion

PET film is easily available Commercial-Off-The-Shelf (COTS) product. The PET films are used in a variety of applications, e.g. printing, labeling, decorating etc. PET film has a good balance of properties, which allows larger operating windows for temperature and tension controls. The properties of typical plastic film are listed in Table 1. PET film has properties such as it can withstand high processing temperature, excellent for high-tension conversion processes, highly durable usage and the highest service temperature, self-extinguishing flammability, and fully functional to  $-70$   $^{\circ}\text{C}$ . PET also has good chemical resistance against acids, ethanol, ketones, carbonate, DMF, *N*-methyl-pyrrolidone [25]. The above mentioned properties of PET film are encouraging for its application as structural material in lithium batteries.

Current materials for current collector in lithium batteries are aluminum and copper. The properties of these two metals are listed in Table 2. The current collectors, namely aluminum foil and copper foil, take roughly about 15–20% by weight and 10–15% by cost of a lithium battery [23]. Graphene is from Ningbo Smallsheet Company, its price is \$100 per kilogram. The content of graphene is 2  $\text{g m}^{-2}$ . The weight and cost will decrease by using graphene-coated PET film as current collectors in lithium ion batteries. Fig. 1a shows photo of PET film COTS product. It is very easily available. Fig. 1b shows photo of a sheet of PET film, it is a transparent film. Fig. 1c and d shows photo and SEM image of G-PET film, respectively. The graphene is uniformly coated on the surface of PET film.

Fig. 2 shows the SAPN electrode with G-PET film current collector and stack cell with laminated soft package. The electrode looks smooth and flat, as shown in Fig. 2a. It becomes a little bit curl after compaction due to one side coating, as shown in Fig. 2b. One layer stack cell with lithium foil anode is assembled using

**Table 1**  
Comparative data of typical plastic films.

Property	Unit	PET	BOPP	PE	PVC	Nylon	PC
Specific gravity	$\text{g cm}^{-3}$	1.40	0.91	0.92	1.40	1.15	1.15
Elongation	%	120	110	400	50	100	140
Melting point	$^{\circ}\text{C}$	260	170	135	180	223	240
Tensile strength	$\text{kgf mm}^{-2}$	22	19	2	10	22	10
Tear strength	$\text{kgf}$	22	15	2	8	20	10
Insulation breakdown	$\text{kV}$	6.5	6.0	4.0	4.0	3.0	5.0
Dielectric constant	0.1 kHz, 25 $^{\circ}\text{C}$	3.2	2.1	2.3	3.0	3.8	3.0
Service temperature range	$^{\circ}\text{C}$	-70 to 150	-40 to 120	-50 to 75	-20 to 80	-70 to 130	-100 to 130

Note: PET – Polyethylene terephthalate; PE – Polyethylene; PVC – Polyvinyl chloride; PC – Polycarbonate; BOPP – Biaxially-oriented polypropylene; Nylon–Polyamide. Data sources: <http://www.ampef.com/chart.html>.

Download English Version:

<https://daneshyari.com/en/article/7740925>

Download Persian Version:

<https://daneshyari.com/article/7740925>

[Daneshyari.com](https://daneshyari.com)