



Electrochemical performance of pyrolyzed polyacrylonitrile (PAN) based Sn/C composite anode for Li-ion batteries

Won-Seok Chang^a, Cheol-Min Park^b, Hun-Joon Sohn^{a,*}

^a Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea

^b School of Advanced Materials & System Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 730-701, Republic of Korea

ARTICLE INFO

Article history:

Received 23 September 2011

Received in revised form 17 February 2012

Accepted 27 February 2012

Available online 6 March 2012

Keywords:

Polyacrylonitrile (PAN)

Sn/C composite

Li-ion batteries

Anode materials

ABSTRACT

The electrochemical behaviors of pyrolyzed polyacrylonitrile (PAN) were investigated to be applied as a carbon source in a metal–carbon composite anode in Li-ion batteries. Pyrolyzed PAN showed a porous structure with a reversible capacity approximately 300 mA h g^{-1} . A pyrolyzed PAN based Sn/C composites were synthesized from SnO and PAN using a high energy ball milling followed by carbothermal reduction, and the Sn particles with diameters of 100–200 nm were randomly embedded on the carbon matrix. The composite electrode exhibited a relatively large capacity and an excellent cycle behavior. The enhanced electrochemical performances of this composite were attributed to the role as a matrix and porous nature of pyrolyzed PAN which accommodated a large volume expansion of the Sn during the reaction with Li, the increased electrical conductivity of pyrolyzed PAN and the uniformly dispersed nanometer sized Sn that formed during the cycling.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Li-ion batteries are one of the most viable power source alternatives in various fields because of their high energy density, which can be suitably applied to small electronics (i.e. cell phone, laptop computer, etc.). Nowadays, technology is becoming more advanced, and their usage is being expanded to electric vehicles (EVs) and back-up electricity storage units for renewable energy sources.

Much effort has been focused on Li-alloying materials with a higher capacity than graphite anodes [1–3] because the currently available commercial graphite anodes have a limited theoretical capacity of 372 mA h g^{-1} (LiC_6). Alloy systems such as Li–Si ($\text{Li}_{4.4}\text{Si}$: 4198 mA h g^{-1}) [4,5], Li–Sn ($\text{Li}_{17}\text{Sn}_4$: $959.5 \text{ mA h g}^{-1}$) [6–8], Li–Sb (Li_3Sb : 660 mA h g^{-1}) [9–11], Li–P (Li_3P : 2596 mA h g^{-1}) have been suggested [12,13]. Although these systems exhibit a larger theoretical capacity than graphite, their cyclability rapidly fades, hindering their applicability as a replacement for the graphite anode because of the huge volume expansion/contraction that occurs during the Li insertion/extraction. Thus, the volume expansion is one of the key factors, which must be alleviated to be utilized for these advantageous alloy systems.

Polyacrylonitrile (PAN, $[\text{C}_3\text{H}_3\text{N}]_n$) is a highly crystallized polymer that has been used as a carbon fiber source. Its melting temperature is 319°C , and it is known to become a porous structure

when it is sustained at a high temperature [14–16]. Materials with porous structures are advantageous to electrode materials for Li-ion batteries. The porous structures offer a large contact area for the electrolyte with a high rate capability and play a role as a buffer for the volume expansion of the electroactive materials [17,18]. Additionally, an enhanced electrical conductivity has also been observed for pyrolyzed PAN at various heat treatment temperatures [19]. Pyrolyzed PAN anodes have been tested as an anode material for Li ion batteries [19–21], but they have a reversible capacity of less than 300 mA h g^{-1} with a poor cyclability. Although metal (Sn,Si)/PAN composites [22,23] or Sn/C [24,25] composites have also been investigated in order to increase the reversible capacity, these materials still suffered from capacity fading during the cycling, and/or their synthesis processes were complicate.

In this work, electrochemical behaviors of a pyrolyzed PAN were investigated to be used as a carbon source (matrix) and the pyrolyzed PAN based Sn/C composite was simply prepared using a high energy mechanical milling (HEMM) followed by a carbothermal reduction in order to increase the reversible capacity as well as to enhance the cyclability. This pyrolyzed Sn/C (PAN) composite was tested as an anode material for Li-ion batteries and compared to a pyrolyzed PAN anode.

2. Experimental

To obtain a pyrolyzed PAN, a PAN ($[\text{C}_3\text{H}_3\text{N}]_n$, Aldrich) powder was heat-treated at 900°C for 3 h under an Ar atmosphere and

* Corresponding author. Tel.: +82 2 880 7226; fax: +82 2 885 9671.

E-mail address: hjsohn@snu.ac.kr (H.-J. Sohn).

then cooled to room temperature. The heat-treated sample was ground and tested as an anode material. Also, a pyrolyzed Sn/C (PAN) composite was synthesized using the following method. SnO (Aldrich, +99%, 10 μm), PAN and two different sizes of steel balls (3/8 in., 3/16 in.) were placed into a hardened steel vial with a capacity of 80 cm^3 at a ball/powder ratio of 20:1. HEMM process was conducted at 800 rpm under an Ar atmosphere for 6 h. The mixture of SnO and PAN powders was carbothermally reduced under the same conditions (900 $^\circ\text{C}$, Ar atmosphere, and 3 h) in order to produce the pyrolyzed Sn/C (PAN) composite. The preliminary studies showed that the optimal ratio of SnO to PAN for the pyrolyzed PAN based Sn/C composite was 1–5 by weight for the best electrochemical performance.

The pyrolyzed PAN and the pyrolyzed Sn/C (PAN) composite were characterized using X-ray diffractometer (XRD, Rigaku D-MAX 2500, $\text{CuK}\alpha$ radiation), scanning electron microscope

(SEM, JEOL JSM 6360), focused ion beam (FIB, SMI3050SE) using Ga^+ ion beam (max. ion current: 20 nA), and high-resolution transmission electron microscope (HRTEM, JEOL 3000F) operating at 300 kV and an element analyzer (FLASH, EA1112, Thermo Electron Corp.). For the TEM observations, a dilute suspension of the sample was dropped onto a carbon-coated TEM grid and dried in a vacuum chamber for 3 h.

The electrodes were prepared by coating a slurry of the active material (pyrolyzed PAN or pyrolyzed Sn/C (PAN) composite, 70 wt.%), Super P as a conducting agent (15 wt.%) and polyvinylidene

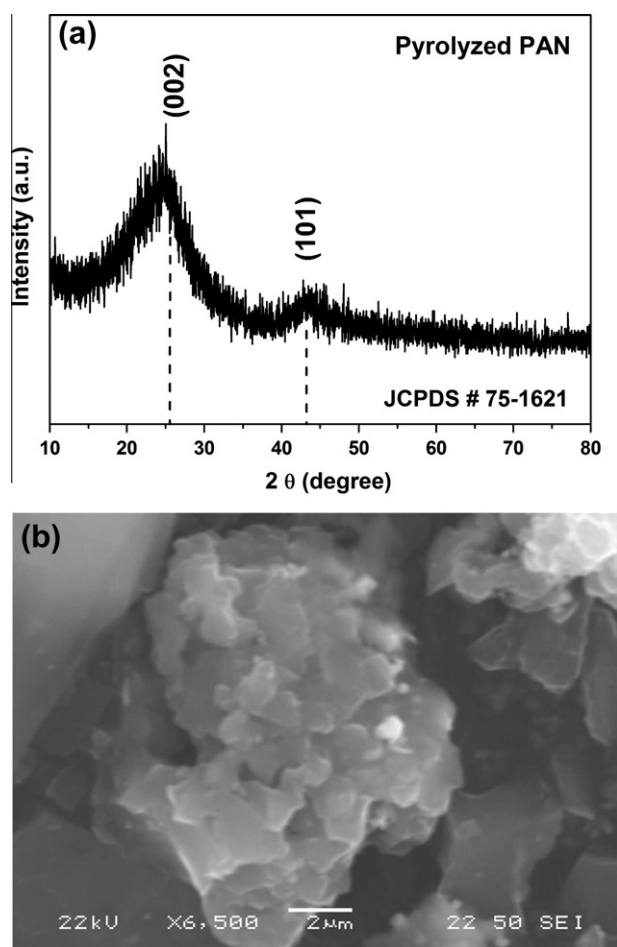


Fig. 1. Characterization of pyrolyzed PAN: (a) XRD pattern of pyrolyzed PAN and (b) SEM image of pyrolyzed PAN.

Table 1
Elemental analyses of the pyrolyzed PAN and pyrolyzed Sn/C (PAN) composite.

	Pyrolyzed PAN	Pyrolyzed Sn/C composite
Element (wt.%)	C (84.8%) N (11.1%) H (0.5%)	Sn (28.8%) C (65%) N (5.8%) H (0.4%)

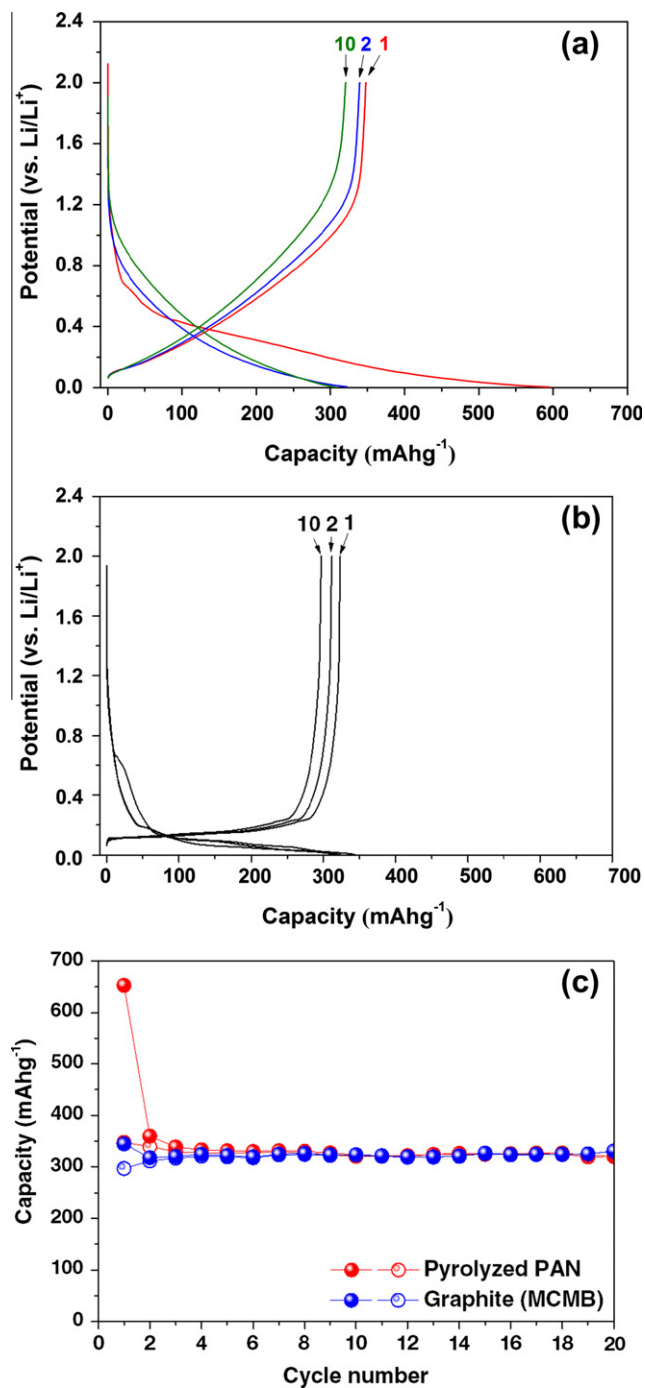


Fig. 2. Electrochemical performances of carbon-based electrodes: (a) voltage profile of pyrolyzed PAN, (b) voltage profile of MCMB electrode and (c) cycle performances of pyrolyzed PAN and MCMB electrodes.

Download English Version:

<https://daneshyari.com/en/article/219388>

Download Persian Version:

<https://daneshyari.com/article/219388>

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