INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–9

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Bundle-type silicon nanorod anodes produced by electroless etching using silver ions and their electrochemical characteristics in lithium ion cells

Jung Sub Kim [a,b], *Hun-Gi Jung* [a], *Wonchang Choi* [a], *Haw Young Lee* [a], *Dongjin Byun* [b], *Joong Kee Lee* [a,*]

[a] *Advanced Energy Materials Processing Laboratory, Center for Energy Convergence Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea*

[b] *Department of Material Science & Engineering, Korea University, Seoul 136-713, Republic of Korea*

ARTICLE INFO

Article history:
Received 28 September 2013
Received in revised form
20 January 2014
Accepted 1 February 2014
Available online xxx

Keywords:
Silicon
Electroless etching
Metal-assisted chemical etching
Anode
Surface modification

ABSTRACT

This study investigates bundle-type silicon nanorods (BSNR) that are aimed at improving the discharge capacity and life cycle characteristics of secondary cells, by controlling the shape and etching depth of silicon thick-films produced by electroless etching. The prepared BSNR structure is composed of a columnar bundle, having a diameter of 100 nm and lengths of 1.5 and 3.5 μm. The etching depths of the nanorods have a significant effect on the electrochemical performance characteristics, including the capacity fading and coulombic efficiency. Using a BSNR electrode therefore allows for an anode with a high capacity and efficiency in lithium ion cells, and can help overcome the issues associated with conventional silicon thick-films. Furthermore, as a result of its unique self-relaxant structure, electrode deterioration is improved through mitigation of the volume change.

Introduction

The power sources for portable electronics such as mobile phones, notebook computers, and personal digital assistants (PDAs) not only require miniaturization, but also need to be highly energized through having a high energy density. Interest in such energy applications is ever increasing, and secondary cells are becoming more commonly used for hybrid electric vehicles (HEVs). Consequently, silicon is being increasingly used as an anode material for lithium secondary cells as a replacement for more conventional carbon materials [1].

At present, the graphite materials that are commonly used have a theoretical capacity of 372 mAh g^{-1}, whereas that of silicon is about 4200 mAh g^{-1} [2]. However, when silicon is fabricated into an anode, the resulting cell has a charging capacity of only about 3260 mAh g^{-1}, a discharge capacity of 1170 mAh g^{-1}, and a coulombic efficiency of 35% [3]. Furthermore, when the cell is continuously charged and discharged over five cycles, its discharge capacity rapidly decreases to about 300 mAh g^{-1}, or about 10% of its initial value. The reason

* *Corresponding author*. Tel.: +82 2 958 5252, +82 10 8717 0978 (mobile); fax: +82 2 958 5229.
E-mail addresses: leejk@kist.re.kr, joongkee57@naver.com (J.K. Lee).
0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2014.02.007

Please cite this article in press as: Kim JS, et al., Bundle-type silicon nanorod anodes produced by electroless etching using silver ions and their electrochemical characteristics in lithium ion cells, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.02.007

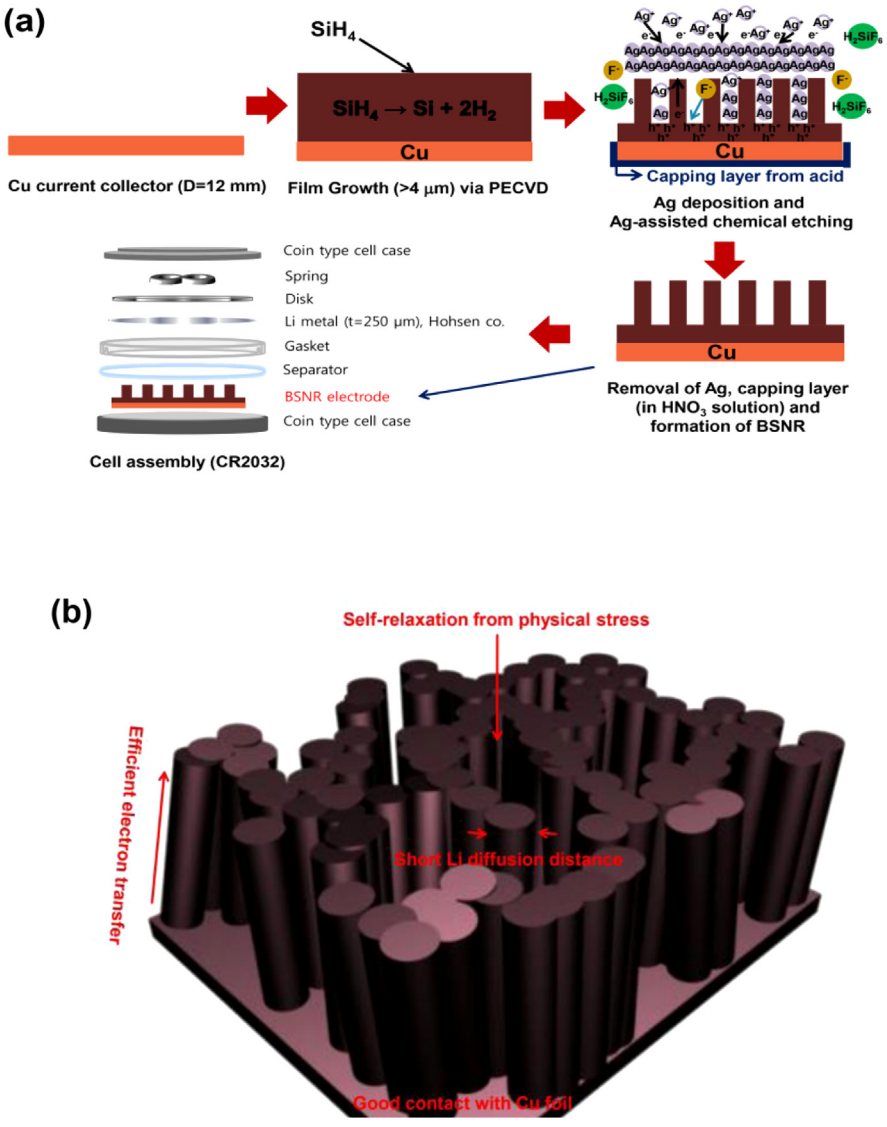

Fig. 1 – Schematic illustration of BSNR electrode (a) Processes for preparation of the BSNR electrode, and (b) features of BSNR prepared by metal-assisted chemical etching.

for this rapid decrease is that the insertion of lithium forms a Li–Si alloy ($Li_{22}Si_5$), which in turn causes a four-fold volume expansion. This results in a breakdown of the silicon structure and blockage of the electron pathway, ultimately causing the formation of a dead volume and a reduction in the silicon anode's capacity. Consequently, as the cell is continuously charged and discharged, its total capacity is rapidly reduced. This phenomenon occurs regardless of whether it is a bulk silicon film, or micrometer-size particles [4].

Various methods have been previously proposed to solve these problems. For example, silicon has been grown on the surface of an electric accumulator in the form of a wire, and then used as an electrode. This method proved advantageous in that electrons could move more easily than in a conventional thin film, and the inner stress of the silicon during the charging and discharging of a cell is less than that of a conventional thin film. Overall, these advantages resulted in an excellent cycle performance. However, despite these strong points, such electrodes cannot be used in practical applications because their performance is based on a thin-film forming process [5].

A method of controlling shape has also been proposed, in which silicon nanoparticles were formed into hollow silicon-nanospheres to overcome the inherent weaknesses of silicon nanoparticles in cycling. However, this method proved to be problematic in that much time is needed to form the hollow silicon nanospheres, and the process itself is quite complicated [6].

In yet another approach, a composite of silicon and silica was first formed, and then just the silica was removed by chemical etching to form bulk silicon particles with numerous pores. This was aimed at overcoming the weaknesses of conventional bulk silicon particles in cycling, and differs from conventional methods in that the pores produced help alleviate volume expansion. However, this method also presents problems in terms of the length of time needed to form the

Please cite this article in press as: Kim JS, et al., Bundle-type silicon nanorod anodes produced by electroless etching using silver ions and their electrochemical characteristics in lithium ion cells, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.02.007