FABRICATION OF SILICON NANOWIRES USING ANODIC ALUMUINUM OXIDE TEMPLATE

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1 Introduction

Recently, due to global warming and the depletion of fossil fuels, environmentally friendly renewable energy is an increasing need for development [1]. So, the development of high storage required for efficient use of energy; lead acid, nickel cadmium, nickel metal hydroxide, and other rechargeable batteries (Fig. 1) [1]. Especially, lithium-ion (Li-ion) battery has been attracting for next-generation energy capacitor, which has greatest electrochemical properties, such as high power and energy density [2]. Therefore, it is applied to in renewable power sources and portable electronics; mobile phone, lap-top computer and electric vehicles (EV) [2-5].

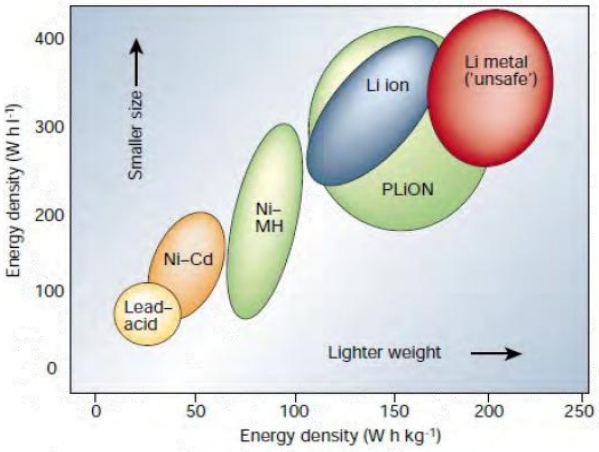


Fig.1. Comparison of battery technologies including volumetric energy densities and gravimetric energy densities [2].

Basic Li-ion battery is composed of anode, cathode, electrolyte, and separator, and its capacity depends on anode material [6]. In several decades, many researchers have study for preparing anode of Li-ion battery using C, Sn, Sb and Si [7-9]. Especially, silicon based materials have high theoretical capacity (~4200 mAh/g per weight and 10 times more than carbon materials), and is attracted as the anode [10,11]. However, silicon materials have large volume change during the lithium insertion/extraction, which have limited application. In an attempt to overcome this problems, Si anodes have been prepared with micron-sized particles, nano-sized particles, and silicon nanowires (SiNWs) [12,13].

In this study, SiNWs was fabricated by templating method using anodic aluminum oxide template (AAO). After reported as 1995s, AAO template has been widely used as template for preparing various nanostructures [14]. AAO template can easily control pore diameter and length by controlling anodizing control, and has great reproducibility. As these properties, AAO template is known as great tool for preparation of SiNWs.

2 Experiment

2.1 Fabrication of Anodic Aluminum Oxide Template

The AAO templates were fabricated by a two-step anodizing method [14,15], as shown in Fig. 2. The high-purity aluminum foil was cut into 2.5×5 cm^2. Prior to the electrochemically process, the aluminum foil was degreased with acetone and rinsed in deionized water. And then, aluminum foil was annealed in 500^oC for 5 hr. Subsequently, the foils were degreased in 0.1 M NaOH and 0.1 M HNO_3 at 40^oC for 5 min, rinsed with deionized water and then electropolished in a 1:4 by volume mixture of $HClO_4$ and C_2H_5OH at 20 V for 30 sec. First anodizing process carried out under constant voltage at 40 V in a 0.3 M oxalic acid for 1 hr at 0-^oC. Then chemically removal of the anodic oxide layer was carried out in a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid. Second anodizing process was carried out with same condition of first anodizing for 45 min. And then pore widening process, namely, AAO was treated with a 0.1 M phosphoric acid at 30^oC for 1 hr.

2.2 Fabrication of SiNWs using AAO

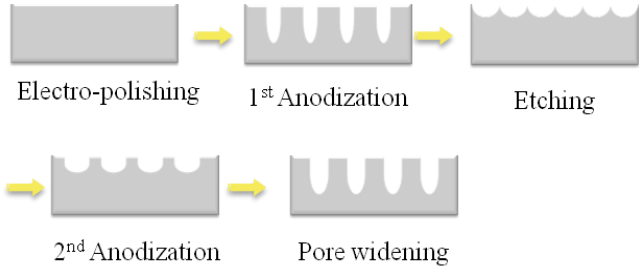


Fig.2. Schematic of fabrication of anodic aluminum oxide template.

Silicon nanopaticles (SiNPs) was synthesized by published method [16]. At first, butyl-capped Si gel was prepared using reduced Si ion ($SiCl_4$) and sodium-naphthalide at room temperature. And then, prepared solution having dark-brown color was mixed with 1,2-dimethoxyethane. The resulting solution was heated at reflux at 400°C for 9 hr. This solution was mixed with butyllithium and stirred overnight. The solvent and naphthalene were removed by using a rotary evaporator and by heating under vacuum at 120°C, respectively, and NaCl and LiCl by-products were removed by partitioning between excess n-hexane and water. The final product was a pale-yellow viscous gel, namely, butyl capped silicon nanoparitcles were prepared [16]. And then, it was impregnated in AAO template with precursor, through processing of high-temperature calcinations.

2.3 Characterization

The morphology of the AAO was confirmed by scanning electron microscopy (SEM). The result of SEM showed the AAO of diameter, and length. The composition and structure of the Si nanowires were investigated by Energy dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD) pattern, respectively. Its electrical properties were analyzed by cyclic voltammetric (CV).

3 Results and Discussion

The charge and discharge reactions in the lithium-ion battery are based on the Li+-ion transfer between positive and negative electrodes via lithium-ion electrolyte [17]. Charging/discharging reactions are reversible (Fig. 3):

Cathode :

$$LiCoO_2 \leftrightarrow xe^- + Li_{(1-x)2} + xLi^+ \quad (1)$$

Anode :

$$xLi + 6C + xe^- \leftrightarrow Li_xC_6 \quad (2)$$

Overall :

$$Li^+ + LiCoO_2 \rightarrow Li_2O + CoO \quad (3)$$

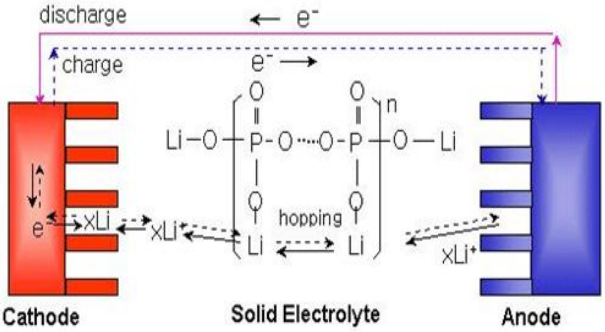


Fig.3. Schematic of lithium-ion battery.

Silicon based anode materials have the disadvantages of volume expansion more than 400% for insertion/extraction process of Li-ions. Because 20 nm of SiNPs easily penetrated into AAO pore of 60 nm to 80 nm, and then, SiNWs volume change can be controlled in the AAO pores. Therefore, SiNWs volume change can be controlled in the AAO pores (Fig. 4). We are expecting volume change by lithium ion insertion/extraction using high resolution trans-mission electron microscopy (HRTEM) and Brunauer–Emmett–Teller (BET) analysis.

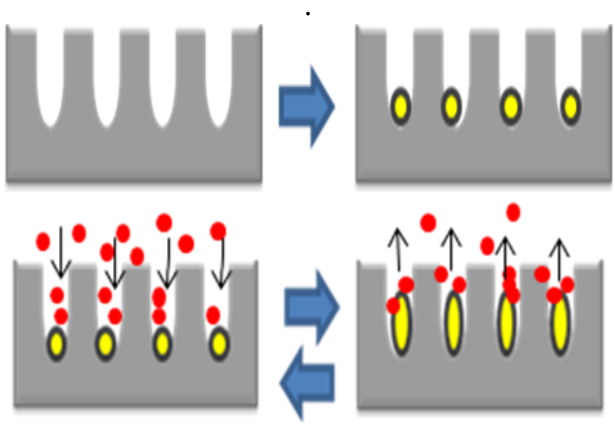


Fig.4. Schematic of silicon nanowires shape and volume changes in AAO template from lithium ion insertion/extraction.

The AAO template has fabricated by the two anodizing steps for fabrication of SiNWs. The AAO has structured uniformly pore array though the self-assembly process under anodizing condition as shown in Fig. 5.

And the pore size has depended on the pore-widening time. When AAO was prepared with pore-widening for 30 min, the pore diameter showed range of 60 nm, and the pore size of 60 nm for 1 hr,

as shown in Fig. 3(a) and (b).

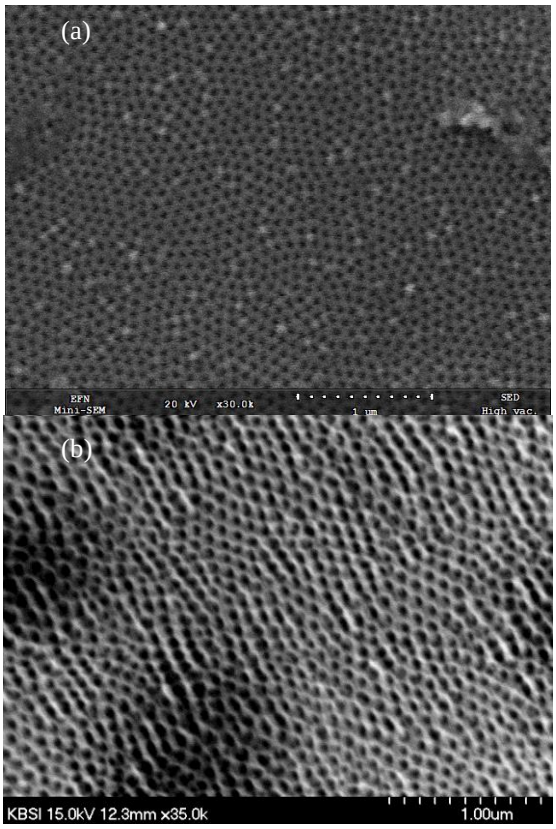
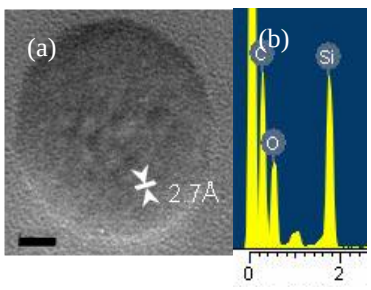


Fig. 5. SEM images of AAOs with average pore diameters of (a) 60 nm and (b) 80 nm.

SiNPs was prepared solution reduction $SiCl_4$ method. The morphology of the SiNP was confirmed by high resolution scanning electron microscopy (HR-TEM). The lattice fringes (2.7 Å) are consistent with the {111} crystal plane of diamond structured SiNP, and its composition of butyl-capped was confirmed by EDS analysis (Fig. 6).



Atom	Atomic %
C	64.14
O	21.19
Si	14.67

Fig.6. HRTEM image of (a) SiNP (scale bar = 5nm) and (b) EDS analysis data.

Because of SiNPs was dispersed evenly at liquid condition, it has greatly improved the development of anode materials for high-density li-ion battery.

In summary, silicon based materials have attracted used as anode materials for lithium-ion battery. To control of volume change of silicon during li-ions' insertion/extraction, the anodic aluminum oxide was used as template. AAO was showed uniform pore size; 60 nm to 80 nm. 10 nm of SiNPs was impregnated AAO pore. It was control of volume change of silicon nanowires during Li ion insertion/extraction. This result is expected to apply to develop of anode material for lithium-ion battery.

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