LI-ANODE NANOCOMPOSITE USING POROUS SILICON NANOPARTICLES

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ABSTRACT

Lithium Ion Batteries are in great demand because of their high energy storage capability. But they have slow charging and discharging time, also the lifetime of lithium ion batteries is about 1000 cycles, whereas Silicon nanoparticles can be used for upto 10000 cycles retaining the same efficiency. Silicon Nanparticles are attractive for use as anode in lithium ion Batteries as it has low discharge potential. Silicon Nanparticles were synthesized by sol-gel method by using Tetraethylorthosilicates. the obtained silicon Nanoparticles were doped with Boron and facile electrolysis Etching was performed. Porous silicon nanoparticles are a prospective candidate for lithium-ion battery anodes, as the pores can provide additional space for volume expansion of silicon during the charging process, which will help to retain the structural integrity of silicon and prevent large capacity degradation

KEYWORDS: Porous Silica, Nanomaterial, XRD, CV, SEM

INTRODUCTION

The last decade, demand on development of Lithium-ion batteries and high energy storage devices having long life has increased sharply. The electrode of the lithium ion batteries has from low specific capacity[1]. Graphite is generally used as a anode material in Lithium-Ion batteries. Graphite has a specific capacity of 372 mA·h/g which is quite low. Silicon has a high specific capacity (3600mA.h/g theoretically) compared to graphite[2]. Thus it can be considered an alternative to it. The porous silicon nanoparticles find many applications including Lithium ion batteries[3], bio medical imaging, and thermo electric devices. The Porous Silicon nanoparticles are synthesized by wet Eitching of doped silicon wafer with Acid. Lithium-ion batteries life time, voltage, energy density and safety are depend upon Choosing anode material. During the lifetime of the battery capacity declines due to reagregation of SiO2. There is a change in volume during insertion and extraction of lithium in silicon. Significant progress has been made by using silicon Nanoparticles[4],

The structure of silicon are also makes improvements in storage capacity of the electrons when it is used as a anode material. The porous silicon has hollow structure which provides additional space in between silicon as which provides by volume expansion of silicon during the charging process which will help to retain the structural integrity of silicon and prevent large capacity degradation[5]. The synthesis of porous silicon nanoparticles is cost efficient compared to silicon nanowires, silicon nanorods and silicon nano ribbions. In this report we synthesize porous silicon nanoparticles nanoparticles of size38nm. The Ag coating improves the performance of the nanomaterial, this anode material provides good electrochemical properties such as improve in life cycle, reversible capacity, and good performance [6-10].

The fabrication of porous silicon nanoparticles is silicon nanoparticles are doped with Boric Acid and Nitric Acid and annealed at 1000 deg for 2 hours and treated with Etchant solution for etching of silicon and again annealed for 600 deg for 1 hour. The obtained Porous silicon nanoparticles quantity will be in 30% of the total Silicon material, remaining

all material will be washer up by nitric acid and absolute ethanol.

Porous Silicon Nanoparticles can be used as lithium ion batteries as the pores give extra space for volume expansion of silicon which happens during the charging process, helping in preventing large capacity degradation and also preserving structural integrity of silicon. Porous Silicon nanowires and nanorods can also be used, but it is very expensive to synthesise them. Thus porous silicon nanoparticles give a cheaper material.

MATERIALS

Tetraethyl Orthosilicate (teos 98%) was obtained from the sigma Aldrich, ammonium hydroxide solution 31.5% (NH3) was used as received from the Aldrich Company, Absolute ethanol 99 % from Sigma Aldrich Company, Boric acid from Sigma Aldrich Company, Silver nitrate AgNo3 from Sigma Aldrich Company, Nitric acid from Sigma Aldrich Company, Sulfuric acid (H2SO4) from Sigma Aldrich Company Phosphoric acid (H3PO4) from Sigma Aldrich Company.

Preparation of Silica Nano-Particles

Synthesis of silicon Nanoparticles was done by Solgel method using precursor as a TEOS in ethanol, and in presence of ammonia as catalyst [11]. First, 60ml of Absolute Ethanol, 15ml deionized water were stirred for 5 minutes then Ammonia is added 0.5ml by maintaining PH value of 10.5. Then a 5 ml of TEOS in 5ml of Absolute Ethanol was added to the above solution and kept it for 24 hours at temperature 15 °C, white colour gel is formed, thereafter the colloidal solution was separated by high-speed centrifuge, and the silica particles were washed by absolute ethanol to remove undesirable particles and then by drying in oven at 100 °C for 2 hrs white colour powder is formed and again washed with ethanol and heated to 150degree the result obtained is silicon nanoparticles[12].

Doping of Porous Silicon Nano-Particles

The porous silicon Nano-particles were synthesized by doping silicon with boron, and then etched etchant solution. In the first process 1.0g of silicon Nano-particles (synthesis by W. Stober et al., 1968; K.-S Chou and C.-C. Chen, 2006) and various amount of boric acid 0.5, 0.7 gram were well mixed in Nitric Acid solution, and annealed at 1000 °C for two hours. The powder was washed with ethanol and de-ionized water to remove by products such as B2O3 and SiO2. As obtained boron doped silicon Nano-particles were then immersed in 20 ml of etchant solution containing 0.2gm of silver nitrate and 15 of Nitric Acid stir for 15 minutes. DI water is added to the solution and centrifuged at 10000 rpm of 15 minutes and then washed using DI water. The amount of porous silicon is obtained after the heat treatment is about1/3 of the amount of nanoporous silicon[13-16]. After boron doping the final product is only 1/3 of the initial silicon nanoparticles.
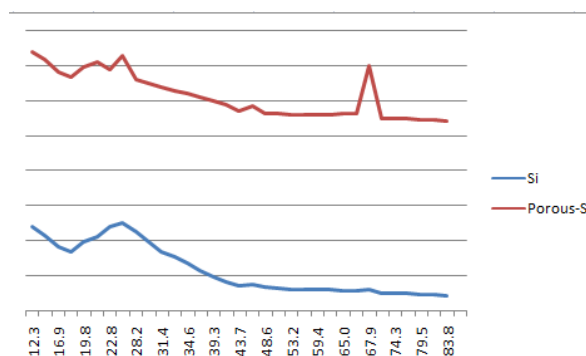
RESULTS AND DISCUSSIONS
XRD

Figure 2: XRD Graph

XRD gives the purities and impurities present in the sample. Each peak corresponds to a different type of material in the graph. The graph given below shows the XRD characterization of the two samples: 1. Silicon Nanoparticles 2. Boron doped porous Silicon nanoparticles. The XRD shows that the particle structure is amorphous.

The purity of the chemicals used for synthesis plays a major role in determining the purity of the silicon nanoparticles. The XRD pattern does not show any Si-B impurities in the graph. It also shows that silicon nanoparticles are doped on 4,0,0 plane. These planes are present because of anisotropic etching of silver ions in "1,0,0" orientation. [reference to scalable paper]

According to literature survey, boron doping is an important step in etching silicon to give the porous nanostructure. Thus the effect of dopant concentration can provide us a relationship to the final structure. Thus we can produce silicon nanoparticles depending on structure required. By using a simplified one dimensional diffusion equation, the highest peak represents reflection from lattice point(1,1,1). The peak of 220 shows reflections from lattice point (220) [17].

$$C(t) = \int C_s \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2}{\sqrt{\pi}} C_s \sqrt{Dt}$$

where $C(t)$ is the total boron concentration, C_S is the surface concentration of boron atoms, and D is the diffusion coefficient.

SEM

According to experimental data it was observed that higher doped silicon nanoparticles resulted in larger pores, leading to rougher surfaces. This can be explained that increasing the dopant concentrations in p-type silicon decreases the energy barrier for electron transfer from silicon to silver, thereby generating large pores.
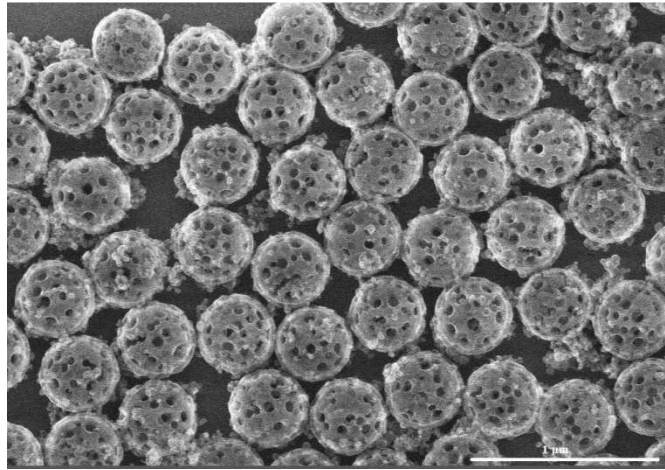
Figure 2: SEM Image

The SEM images of porous silicon nanoparticles show that the particles are spherical in shape with pores on the surface of particles. Thus proving that these are porous silicon nanoparticles. These pores are due to the etching using Boron. It is done to decrease the energy barrier so that electron can pass through the barrier
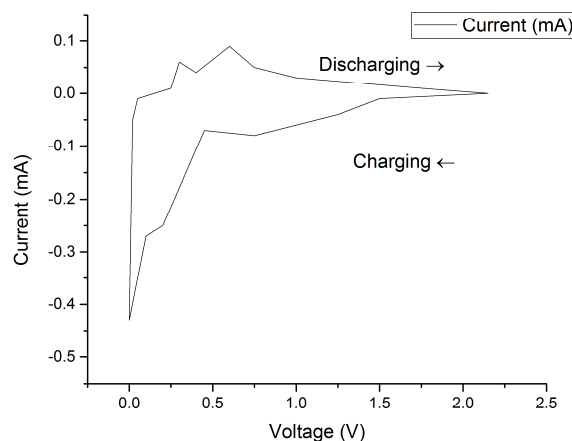
CV TEST

Figure 3: Cyclic Voltammetry Curve

Figure 3 represents the Cyclic Voltammogram of the Porous Silicon Nanoparticles. The graph shows the characteristics of silicon during lithiation and delithiation stages. The Solid Electrolyte Interface layer is proven by the peaks and throughs at 0.5-1.0 V. The peak at 0.2 V represents the formation of amorphous silicon.

CONCLUSIONS

We reported that porous silicon nanoparticles were synthesis by Sol-Gel method and then Doped with Boric acid and electrolysis and acid etching. It is a perfect material for Li-ion batteries. Porous silicon nanoparticles have a hollow structure, having space in silicon that other particles can occupy. This provides large volume expansion during charging process. These porous silicon nanoparticles are produced in cost effective method compared to nanorods and nanowires. We can also add CNT and RGO to study the change in properties. The Boron doped Silicon Nanoparticles can be

combined with RGO and MWCNT's that can accommodate large elastic and electrically conductive matrix. The electrochemical properties can improved by dispersing CNTs uniformly in the interstitial-spaces of Si and carbon materials.

ACKNOWLEDGMENTS

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