



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: [www.elsevier.com/locate/jiec](http://www.elsevier.com/locate/jiec)



## Effect of electron beam irradiation on the capacity fading of hydride-terminated silicon nanocrystal based anode materials for lithium ion batteries

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### ARTICLE INFO

#### Article history:

Received 4 January 2017  
Received in revised form 28 March 2017  
Accepted 1 April 2017  
Available online xxx

#### Keywords:

Lithium ion battery anode materials  
Hydride-terminated silicon nanocrystal  
Polyvinylidene fluoride  
Electron-beam irradiation  
Cross-linking

### ABSTRACT

The selection of binder is extremely important in silicon based lithium-ion batteries (LIBs). Polyvinylidene fluoride (PVDF) has been used as a commercial binder. However, it does not accommodate a large change in volume during cell cycling. In this study, we report on the rediscovery of the use of PVDF without additional synthetic processes or further treatment. By utilizing simple and short e-beam irradiation, hydride-terminated silicon nanocrystals (H-Si NCs) and PVDF can be chemically cross-linked each other, and shows an improved cell performance. This result demonstrates a high potential of the e-beam irradiation process on Si-based anode materials in LIBs.

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### Introduction

The research community is currently engaging in extensive efforts to replace graphite in the anodes of lithium ion batteries (LIBs) with new materials that possess higher capacity, energy, and power density. Various approaches have been applied to investigate both carbon and non-carbon materials. Graphite is a carbon-based material that is commonly used as an active material in the anode due to its excellent characteristics, including flat and low working potential, good cycling ability and low cost [1]. However, graphite allows intercalation of only one Li-ion with six carbon atoms, and this leads to an equivalent reversible theoretical capacity of 372 mAh/g. Additionally graphite has a low diffusion rate of lithium ions ( $10^{-9}$ – $10^{-7}$  cm<sup>2</sup>/s), which results in a poor power density [2]. Hence, it is unavoidable to replace graphite with new anode materials that have a higher capacity, energy, and power density. Non-carbon candidates include nano-sized silicon, such as silicon nanocrystals (Si NCs), silicon nanoparticles (Si NPs), and silicon nanowires (Si NWs), and these have been studied aggressively as candidate materials for the anode of LIBs due their high theoretical capacity for lithium (4200 mAh/g, Li<sub>22</sub>Si<sub>5</sub>) and small size, ultimately reducing the mechanical stress originating

from the large volume expansion/contraction during lithiation/delithiation [3–11].

However, there are some limitations to the applicability of nano-sized Si as an anode material. Primarily, the large expansion/contraction in volume (~400%) during charge/discharge results in the consecutive pulverization of the anode active materials, thereby induce a poor cyclic life and irreversible capacity. In addition, the formation of Si compounds at the solid electrolyte interface (SEI) inhibits lithiation/delithiation during the cycle [12]. To overcome these issues, Si-based materials need to have the following properties: an optimum surface area accessible to the electrolyte, a short diffusion length for lithium ions, a large space available to accommodate the change in volume, and a high electron conductivity. Although various methods have been developed to facilitate the use of high-performance Si-based anode material, existing methods to manufacture nano-sized Si anode materials still have limitations due to the high cost of raw materials, processing costs, low scalability, and inevitable cost of additive such as conducting carbon black and polymer binders, in contrast with commercial graphite anode materials. In this point of view, Park et al. reported 3-D paper-type Si-carbon nanofiber-composite electrode (Si/CNF-P) as a binder/current collector-free anode for LIBs, which prepared using an electrospinning method [13].

Of various options, the cheapest, most scalable, and most simple route to overcome these issues is to search for a new binder system. For instance, PVDF is a commercial binder used in LIBs, but

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it does not provide competent cyclic stabilities in the Si-based LIB systems because the PVDF binder just attaches to the surface of the Si active material with weak van der Waals forces and does not accommodate a large change in volume during cell cycling. Consequently, finding a new and efficient binder is very important assignment to facilitate production of high-performance Si-based LIBs. In this respect, many researchers have focused on finding or synthesizing new effective binders for Si-based LIB systems. Magasinski et al. reported that polyacrylic acid (PAA) can offer superior performance as a binder for Si anodes due to the higher concentration of carboxylic functional group. Their Si active material was coated with polycarbonate (PC) and was then graphitized at 800 °C under Ar flow [14]. Song et al. reported interpenetrated gel polymer binder synthesized by using in-situ cross-linking of PAA and polyvinyl alcohol (PVA) precursors [15]. Recently, Chen et al. reported cross-linked chitosan (CS) as an efficient binder for Si anode of LIBs. The CS was dissolved in an acetic acid solution, then glutaraldehyde (GA) was injected into this solution. Si powder was mixed with Super P and CS or CS-GA at a weight ratio of 60:20:20 in 2 wt% acetic acid solutions [16]. A further study was performed by Liu and Yang by synthesizing an ideal polymer binder by tuning the electronic structure of the functional groups. The molecular structures of the developed polymers are based on polyfluorene (PF)-type polymers. They synthesized the polymer binder by using a Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst and four kinds of molecules: polyfluorene with octyl side chains, fluorine with triethyleneoxide monomethyl ether side chains, fluorenone, and methyl benzoate ester [17,18]. However, these new kinds of binder require complex and uneconomic synthetic processes to provide efficiency and stability in coin cells. Hence, some groups investigated simple surface modification of PVDF membrane or separator. Kim et al. reported PVDF membrane modified with glycidyl methacrylate (GMA) and sodium sulfite using a radiation-induced graft polymerization technique for unique ammonia removal process [19]. Lim et al. reported the effect of electron beam irradiation on pure PVDF films at the melting temperature by varying the irradiation dose. The PVDF films irradiated at the melting temperature show highly cross-linked characteristics, as confirmed by gel fraction and FT-IR, while the films irradiated at the room temperature did not [20]. And Ahn et al. adopt surface-modified polyethylene separator via oxygen plasma treatment to meet requirements for high performance LIBs [21].

In this study, we report on the rediscovery of the use of PVDF binder. By utilizing simple and short (90 s) e-beam irradiation processes between H-Si NCs and PVDF binder at the melting temperature through partial dehydrofluorination, H-Si NCs and PVDF can be chemically interconnected and then cross-linked with each other without additional synthetic processes or further treatment. This cross-linked network system can accommodate a large volume expansion and can form an optimized SEI layer during lithiation/delithiation. The chemical bond between Si and C minimizes separating the binder from the active materials (H-Si NCs) during cycling. Thereby, the decomposition number of electrolytes on the surface of the H-Si NCs could be controlled to not go further. Consequentially, the H-Si NCs cross-linked through e-beam irradiation show an improvement in cyclic stability and a decrease in resistance relative to those that are not irradiated with the e-beam. To the best of our knowledge, this is the first work that demonstrates the improved physical and electrical properties of anode materials in LIBs based on H-Si NCs and commercial PVDF binder processed with e-beam irradiation.

## Experimental

### Chemicals

Tetraethyl orthosilicate ( $\geq 99.0\%$ ), anhydrous toluene (99.8%), anhydrous methyl alcohol (99.8%), sodium chloride ( $\geq 98.0\%$ ), polyvinylidene fluoride (Typical Mw  $\sim 534,000$ ) were obtained from Sigma-Aldrich and were used as received. Ammonium hydroxide solution (25.0% NH<sub>3</sub> in water) was obtained from Acros Organics, DI-water and magnesium powder (99.6%) were obtained from Alfa Aesar. Hydrochloric acid (35.0–37.0%) and ethyl alcohol (99.9%) were obtained from Duksan (Ansan City, South Korea). Hydrofluoric acid (48.0–51.0%) was obtained from J.T. Baker. Super P Li carbon black, *n*-methyl-2-pyrrolidone (NMP), Cu-foil, Li-metal were obtained from Wellcos Corporation (Gunpo City, South Korea). 1.0 M LiPF<sub>6</sub> dissolved in a 1/2 vol% mixture of ethylene carbonate and ethyl methyl carbonate was obtained from Soulbrain (Seongnam City, South Korea). All chemicals were used without further purification.

### Synthesis of silica nanoparticles (SiO<sub>2</sub> NPs)

Size-controlled SiO<sub>2</sub> NPs were synthesized under a sol-gel reaction that is specifically referred to as the solvent controlled method in this study. The ratio between toluene (non-alcoholic organic solvent) and methyl alcohol to 1:3 is controlled to obtain uniform, spherical SiO<sub>2</sub> NPs [22]. 0.05 mol of tetraethyl orthosilicate (TEOS), 37.5 ml of methyl alcohol (MeOH), and 12.5 ml of anhydrous toluene were mixed with stirring, and then 0.02 mol of ammonium hydroxide solution was added dropwise into the mixture. The ammonium hydroxide solution was used to initiate the sol-gel reaction. Afterward, the mixture was stirred for 12 h at room temperature. After the reaction had been completed, whitish precipitates were formed and collected by centrifugation at 15,000 rpm for 5 min. The synthesized SiO<sub>2</sub> NPs were washed with ethyl alcohol and distilled water 5–10 times to remove the remaining ammonium hydroxide (NH<sub>4</sub>OH) until reaching pH 7. Finally, the synthesized SiO<sub>2</sub> NPs were dried at 80 °C in oven during 12 h and frittered by using mortar. The SiO<sub>2</sub> NPs were obtained as a white powder and are depicted in Fig. S1(a).

### Synthesis of oxide-coated silicon nanocrystals (Si NCs@SiO<sub>x</sub>)

Si NCs@SiO<sub>x</sub> were synthesized via magnesiothermic reduction of SiO<sub>2</sub> NPs [23]. Luo et al. have reported that a large amount of sodium chloride (NaCl) can act as a heat scavenger in the reduction process and can prevent the original changes to the morphology of SiO<sub>2</sub> NPs by surpassing the melting temperature of silicon (1414 °C) [24]. SiO<sub>2</sub> NPs (1.0 g), NaCl (10 g), and magnesium powder (0.9 g) were mixed and ground manually to give a grayish powder, and the mixture was heated at 675 °C (2 °C/min) for 15 h under an argon atmosphere in a quartz tube furnace. After reduction, DI-water was added while stirring to result in a dark brown-colored powder product and was paper-filtered to remove the NaCl. The filtered, dark brown-colored product was treated with hydrochloric acid (10 mL) and distilled water (100 mL) for 5 h to remove the magnesium powder (Mg), magnesium oxide (MgO), and magnesium silicide (Mg<sub>2</sub>Si). In this step, magnesium chloride (MgCl<sub>2</sub>), which formed via HCl treatment of Mg, MgO, and Mg<sub>2</sub>Si can be easily removed by paper filtration. Brown precipitates were obtained via centrifugation at 15,000 rpm for 5 min. The precipitates were washed with distilled water (d-H<sub>2</sub>O) until washing resulted in a neutral pH (ca. 7). Then, the product was washed several times with ethyl alcohol (EtOH) and acetone and was dried at 80 °C in an oven for 12 h to yield Si NCs@SiO<sub>x</sub>. Finally, the Si

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