Journal of Power Sources 304 (2016) 373–383

Contents lists available at ScienceDirect

Journal of Power Sources

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

Effect of silicon configurations on the mechanical integrity of silicon–carbon nanotube heterostructured anode for lithium ion battery: A computational study

Sameer S. Damle [a], Siladitya Pal [b], Prashant N. Kumta [a,c,d,e], Spandan Maiti [a,c,d,*]

[a] *Department of Chemical Engineering, University of Pittsburgh, PA 15261, USA*
[b] *Mechanical and Industrial Engineering Department, Indian Institute of Technology Roorkee, Roorkee 247667, Uttrakhand, India*
[c] *Department of Bioengineering, University of Pittsburgh, PA 15261, USA*
[d] *Center for Complex Engineered Multifunctional Materials, University of Pittsburgh, PA 15261, USA*
[e] *Department of Mechanical Engineering and Materials Science, University of Pittsburgh, PA 15261, USA*

HIGHLIGHTS

- Computational study of mechanical integrity of Si–CNT heterostructured anode.
- Reduction of mechanical constraints reduces void nucleation and growth possibility.
- Si thin film coating on CNT is prone to void growth induced mechanical failure.
- Si droplet configuration is mechanically stable compared to Si coating configuration.

ARTICLE INFO

Article history:
Received 27 July 2015
Received in revised form 4 November 2015
Accepted 6 November 2015
Available online 6 December 2015

Keywords:
Li-ion battery
Silicon
Si–CNT heterostructured anode
Plastic deformation
Void nucleation and growth
Mechanical integrity

ABSTRACT

Heterostructures of silicon and carbon nanotubes (CNT) have been widely studied as Li-ion battery anodes. The focus of the current study is to investigate the role of silicon configurations on the mechanical integrity of the Si–CNT heterostructured anodes during electrochemical cycling. We hypothesize that void nucleation and growth in silicon during electrochemical cycling of Li can induce fracture and eventual failure. To test this hypothesis, we utilized a custom developed multiphysics finite element modeling framework considering the lithium diffusion induced elasto-plastic deformation of silicon. We systematically varied the silicon component configuration and enumerated the stress field within it for one complete electrochemical cycle. Resulting evolution of stress state reveals that reducing the mechanical constraints on Si reduces the plastic flow of the material, and thus possibility of void nucleation and growth. We find that the Si droplet configuration is mechanically stable while the continuous Si coating configuration is prone to void growth induced mechanical failure. Present analysis provides a mechanistic understanding of the effect of Si configurations in heterostructured electrodes on its mechanical integrity, which can help in design of next-generation hetersostructured electrodes with improved capacity retention.

1. Introduction

In the past decade, lithium ion batteries have emerged as the most dominant energy storage device among other battery technologies such as Ni–Cd, Ni–MH, lead acid, etc. Current state of the art Li ion batteries have graphitic anode providing an electrochemical capacity of 372 mAh g^{-1} [1]. Improvement in battery technology is constantly pursued as the demand for energy storage devices is expected to rise in future. Silicon is projected as the most promising anode for Li ion batteries replacing graphite due to its high theoretical gravimetric capacity of 4200 mAh g^{-1}. However, mechanical degradation and eventual failure of Si due to the lithium alloying induced stresses during electrochemical cycling leads to the loss of capacity, thus limiting its cycle life and commercialization [2,3].

In order to address the issue of mechanical failure of silicon as the anode material, size of the active material has been identified as a major factor. Experimental as well as modeling studies have revealed that the use of nano-sized amorphous Silicon (*a*-Si) anode configurations in the form of nanoparticles [4], hollow nanospheres [5], nanowires [6], nanotubes [7], or nanofilm patterns [8] signifi-

---

[*] Corresponding author. 207 CNBIO, 300 Technology Drive, Pittsburgh, PA 15219, USA.

E-mail address: spm54@pitt.edu (S. Maiti).

http://dx.doi.org/10.1016/j.jpowsour.2015.11.027

cantly improve the anode capacity retention over multiple electrochemical cycles. The critical sizes below which mechanical failure can be averted during electrochemical cycling have been identified for these configurations [9–13]. However, *a*-Si suffers from other issues such as poor electronic conductivity and charge transport, significant first cycle irreversible loss, inferior performance at higher charge rates, and low columbic efficiency. On the other hand, multiwall carbon nanotubes (MWCNTs) are known to have very good mechanical strength along with excellent electrical and thermal properties [14–16]. In addition, they exhibit moderate capacity of ~300 mAh g^{-1} following Li intercalation [17]. Thus, core–shell heterostructures comprised of carbon nanotube (CNT) core and nanostructured Si shell that combines the merits of both these anode elements have emerged as a promising candidate for Si based anode for Li-ion batteries.

Many researchers have recently reported synthesis of a Si–CNT core–shell heterostructure consisting of a thin continuous Si coating on the CNT. Hu et al. [18] deposited Si coating on CNT sponge structure by CVD. Electrochemical cycling of the heterostructure in a voltage range of 0.05–1 V showed an impressive first cycle discharge capacity of 3200 mAh g^{-1} with 14% irreversible loss. After 50 cycles, however, the anode capacity faded to 1900 mAh g^{-1}. Formation of nanopores in the Si coating due to the high stresses encountered during electrochemical cycling was determined to be responsible for the capacity fade. Fu et al. [19] observed formation of axial cracks in the Si coating in the Si–CNT heterostructure post electrochemical cycling. In-situ TEM investigation by Wang et al. [20] on a heterostructure comprising of a thin (~13 nm) Si coating adhered to a carbon nano-fiber showed cracking of the Si coating during electrochemical cycling. They concluded that accumulation of damage in the Si coating over prolonged electrochemical cycling to be the mechanism for eventual capacity fade of the anode structure. A similar observation was reported by Sun et al. [21], where they observed the formation of axial cracks along the length of the continuous Si coating on CNT during in-situ electrochemical cycling of the heterostructure. It should be emphasized here that such axial cracks might not cause complete loss of capacity as long as the active material remains adhered to the CNT. For complete capacity fade, substantial loss of electronic contact between current collector and the active material mediated by disintegration of the active component is required.

Experimentalists have tested different strategies to limit the mechanical failure of the Si–CNT heterostructure thus improving its capacity retention, such as: providing sufficient inter-wire spacing [22,23], improving adhesion at the Si–CNT interface [24], coating the Si film on CNT with a thin carbon layer [19,25], and employing a binder free approach by directly scribing the active material onto current collector [26]. Another approach that has been tested to improve the capacity retention of Si–CNT heterostructured anode is by tailoring the geometry of silicon shell to limit the Li alloying induced mechanical degradation. Gohier et al. [27] decorated vertically aligned thin CNTs of 5 nm diameter with 10 nm sized Si droplets. Providing sufficient free space for expansion of Si droplets resulted in a high reversible capacity of 3000 mAh g^{-1} at 1.3C *C-rate* with 90% capacity retention after 37 cycles. Work done in the Kumta group by Wang et al. [28,29] has demonstrated the electrochemical performance of the hybrid Si–CNT heterostructure anode by synthesizing ~40 nm diameter droplets of Si tethered to MWCNT by CVD process. The heterostructure anode showed a steady capacity of ~2000 mAh g^{-1} for 22 cycles. Building on the work of Wang et al. [28,29], Epur et al. [30] varied the morphology of *a*-Si coated on the CNT by changing the flow conditions in the CVD process. The synthesis yielded two different Si geometries in the Si–CNT heterostructure based on the flow conditions: continuous Si film on CNT, and Si droplets deposited on CNT. The heterostructure with continuous Si film showed an initial capacity of ~3200 mAh g^{-1} with 10% first cycle irreversible loss. After 20 cycles the capacity dropped to ~1950 mAh g^{-1}. In case of the heterostructure with Si droplet configuration, an initial capacity of ~2700 mAh g^{-1} with 10% first cycle irreversible loss was observed. However, the capacity fade rate was considerably less and a capacity of ~2340 mAh g^{-1} was retained after 20 cycles. Thus, the electrochemical cycling results consistently demonstrated that the droplet configuration outperformed the film configuration. It can be inferred from the above-mentioned experimental observations that the geometrical features of Si can alter the anode cyclic performance significantly, and thus can be a promising route to design anode configurations with improved cyclic performance. Realization of this feature will however require fundamental insight into the configuration dependent mechanical performance of Si–CNT heterostructures. Motivated by this objective, herein we report the effect of the geometry of the active material in the Si–CNT heterostructures on its mechanical integrity during a single electrochemical cycle. We have resorted to a thermodynamically consistent theoretical framework and its computational counterpart recently developed by us [31–33]. Our methodology considers alloying induced stress and consequent mechanical failure of the electrode material. In the course of this paper, we systematically varied the geometry of the Si film coating on CNT from a continuous Si film to a Si particle in the shape of 1/8th of a nanoring adhered to CNT. Mechanical integrity of the different configurations was analyzed by studying mechanical stress state as well as plastic flow within the active material. Possible nucleation and growth of voids in the plastic solid leading to the mechanical failure of silicon was of particular interest. We demonstrate that the mechanical constraints arising from the adhesion of Si shell to the CNT core, as well as the configuration of the active material itself, is responsible for the mechanical failure of the anode configuration. Providing sufficient free space for Si expansion and thus reducing the mechanical constraints significantly reduces the stresses, thus improving its mechanical integrity during electrochemical cycling. We relate our simulation results to the experimental observations found in the literature whenever possible.

The paper is organized as follows: In Section 2 we briefly describe the basic assumptions and detail the equations of the previously developed theoretical framework. In Section 3, we present the computational methods for the simulation study. Section 4 contains the description of the heterostructure configurations under consideration and the relevant materials properties as well as boundary conditions utilized in the simulations. Results obtained from the simulation studies and a brief discussion on it is presented in Sections 5 and 6, respectively. The conclusions and future directions from the work presented in this research article are summarized in the last section.

2. Theoretical framework

In this section we briefly describe the theoretical framework used to model transport of lithium in silicon and attendant mechanical stress field in the silicon domain. The governing equations of the model are detailed in Table 1. For the definition of each variable, please see the list of symbols provided at the end of the article. The details of the framework can be found in our previously published reports [31–33].

For our simulations, we assumed that the *a*-Si shell contributes primarily towards the overall electrochemical capacity of the anode configuration owing to its order of magnitude higher capacity (~4200 mAh g^{-1}) compared to that of CNT (~300 mAh g^{-1}). Accordingly, we did not consider any Li transport in the CNT core. Electrochemical cycling of the anode heterostructure was carried out under galvanostatic conditions similar to that performed in experiments [30]. The electrochemical reaction was considered at all surfaces of the active material that were exposed to the electro-