



Effects of graphene and carbon coating modifications on electrochemical performance of silicon nanoparticle/graphene composite anode



Rhet C. de Guzman^a, Jinho Yang^b, Mark Ming-Cheng Cheng^b, Steven O. Salley^a, K.Y. Simon Ng^{a,*}

^a Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, USA

^b Department of Electrical and Computer Engineering, Wayne State University, Detroit, MI 48202, USA

HIGHLIGHTS

- Studied the effects of graphene and Si modifications in the battery performance.
- High rate cycles are possible with a good balance of graphene sheet size and disorder.
- Graphene with high pyridinic N resulted in both higher capacity and rate capability.
- PAN-based coating approach resulted in N-doped C coating on Si.
- Si with N-containing coating showed overall capacity retention and rate performance.

ARTICLE INFO

Article history:

Received 8 April 2013

Received in revised form

10 July 2013

Accepted 28 July 2013

Available online 3 August 2013

Keywords:

Lithium ion battery

Silicon nanoparticles

Graphene

Composite anode

ABSTRACT

The effects of graphene and C coating modifications on electrochemical performance of silicon nanoparticle (SiNP)/graphene composite anode were investigated. Graphene with varying sheet sizes (238, 160 and 113 nm) were used as an anode material where a cycling performance dependence on the sheet size (edge sites and sheet disorder) was observed. Temperature-dependent N doping of graphene resulted in graphene with N (5.97% w/w) presenting three binding configurations: 72.1% pyridinic N, 22.4% pyrrolic N and 5.5% graphitic N. The nitrated graphene displayed improved cycling capacity and minimized performance decay, principally due to the pyridinic N. Galvanostatic cycling using increasing current density rates (500–2500 mA g⁻¹) of SiNP composites with C coating/deposition showed improvements in both capacity retention and rate performance. A polyacrylonitrile (PAN)-based coating scheme was used to produce a N-containing (2.20%) C coating which displayed the best high performance improvements, attributable to the minimization of direct solid-electrolyte interphase (SEI) formation and improvement in the conduction path. Optimization of the methods to achieve the best modification characteristics might enable performance improvements that maximize the capabilities of the materials.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The promise of greatly increased anode specific capacity for lithium ion batteries (LIBs), by as much as ten-fold through the substitution of Si (theoretical capacity of 3572 mAh g⁻¹ [1]) for graphite (theoretical capacity of 372 mAh g⁻¹ [2]), has tremendously influenced the direction of secondary battery research.

Likewise, Si's abundance and mature infrastructure further drive this cause. With Si, a high capacity Li alloying reaction produces a Li-rich phase (Li₁₅Si₄) compared with the intercalation reaction with graphite (LiC₆). However, the increased accommodation of Li⁺ during charge–discharge cycles induces large volume variations (as much as 370%) and stress on the bulk anode matrix that ultimately leads to failure. In view of this hindrance, different strategies have been pursued to mitigate this effect including: amorphous thin films [3–6], nanowires [7–9], nanotubes [10], and porous morphologies [11–13]. Despite these advances, capacity degradation during cycling is still problematic, suggesting electrode fracturing

* Corresponding author. Tel.: +1 313 577 3805; fax: +1 313 577 8171.

E-mail address: sng@wayne.edu (K.Y. Simon Ng).

and delamination that leads to eventual electrical contact losses. The most promising recent advances have employed Si nano-sized particles coupled with carbonaceous material [14–22] as a form of support; however, this configuration is not without challenges.

Graphene is such a carbonaceous material that has great potential as a support. Its highly organized sp^2 -bonded C atoms provide outstanding mechanical and electrical properties compared with other known materials [23,24]. It has the potential to assist in the electron conductivity in composite anodes while providing a matrix for the SiNPs. Lately, graphene has been widely used as an anode material that demonstrates capacities even higher than those of current state-of-the-art graphite. Such performance was achieved through the use of disordered graphene (containing imperfections) where Li can be hosted on both sides of the sheets [25,26]. However, increasing the level of disorder also increases the number of edge sites which promote side reactions leading to large irreversible capacity losses. These sites have been proven to be more electrochemically active than the basal plane sites, leading to more electrolyte decomposition [27]. This causes severe breakdown of commercially available electrolyte (e.g., $LiPF_6$ in organic solvents), forming an unstable non-conducting SEI [14,28]. Nitrogen has a stronger electronegativity compared with carbon; its lone pair electrons form conjugated bonds with the graphene π -system, hence it has been widely studied as a dopant to modify graphene's electronic and chemical properties [29,30]. Nitrogen doping of graphene anode materials has resulted in reversible capacities much higher than graphite [28,31]. While it shows much promise, it has not yet been explored in standalone graphene anode materials.

Nano-sized Si particles benefit from having high surface area, which provides more sites for Li alloying to improve electrode capacity (and rate capability). However this attribute also gives rise to intensive side reactions with the electrolyte (especially $LiPF_6$ species) as reported by Aurbach et al. [32]. These side reactions are the primary source of SEI, which irreversibly consumes Li during formation and ultimately contributes to cell capacity fading. In order to address this, a predominant approach has been used to apply a C-based material to act as a passivation layer. This technique has been used in thin films [33] and clustered particles [15–17]. All have shown varying levels of improvement by minimizing side reactions with the electrolyte; yet it is still a challenge to achieve high cycle life. Employing a N-containing C coating on the SiNP [34,35] to further improve the electrochemical kinetics can potentially surpass plain C coated Si. Since the Li-rich alloying reactions are still the governing reactions with Si-based anode materials, full mitigation of the cycling volume expansion is very difficult to accomplish. Even though SiNPs have increased fracture toughness [36], volume variations are still considerable. Even for particles within the nanometer range, volume expansion (much worse fracturing) of particles due to cycling could lead to successive cycles of SEI rupture and reformation that will lead to further irreversible loss of Li (and capacity). To address these issues, the objective of this work is to explore modification schemes for the components of SiNP/

graphene composite anode in order to improve the cycling performance. The effect of graphene sheet size variation and the effects of nitriding level of standalone graphene anodes at varying temperatures on the charge–discharge performance of the resulting anode were investigated. The SiNP was subjected to C-based coating that is targeted to protect the particles from direct exposure to the electrolyte while improving the conduction network. This modification may potentially avoid the unstable cycle of SEI formation/reformation as the SiNPs are expected to expand. Furthermore, a novel N-containing coating using carbonized PAN was used as a coating material for highly dispersed SiNP. These modifications were coupled with an improved surfactant-assisted particle dispersion procedure that can create a well dispersed particle (and modified particles) within a graphene matrix. Overall, the resulting improvements in cycling performance brought by these modifications may contribute to the further advancement of SiNP-based composite anode design.

2. Experimental

2.1. Graphene modifications

2.1.1. Graphene anode synthesis

Three sources of graphite (Table 1): graphite A (Dixon Microfyne, Ashbury, NJ), B (230U grade, Asbury Carbons, Asbury NJ) and C (2299 grade, Asbury Carbons) with varying flake sizes were used as the graphene precursor to make graphite oxide via a two-stage Hummers' method according to Kovtyukhova et al. [37]. In a series of steps, the graphites were first pre-oxidized and then subjected to strong oxidizing agents to produce the respective graphite oxides. After the Hummers' method proper, graphite oxide suspensions of about 6 mg mL^{-1} were stored in amber bottles at room temperature.

In order to create the graphene anode material, 6 mL of the graphite oxide suspensions were probe sonicated (Misonix, Ultrasonic Cell Disruptor, Farmingdale, NY, 100 W, 22.5 kHz) for 2 h. This step exfoliates the expanded structure of graphite oxide to form the graphene oxide (GO) platelets. All sonics-based steps were performed at room temperature and were closely monitored to minimize temperature increase. The samples were then vacuum-filtered (setup: Millipore 47 mm all-glass vacuum filter holder-funnel and flask; filter: $0.2 \mu\text{m}$ pore, Whatman Anodisc) forming solid GO papers. The resulting structures were then air-dried overnight followed by thermal reduction. The reduction was done in a tube furnace (Series 3429, Applied Test Systems Inc., Butler, PA) using $10\% \text{ H}_2$ in Ar at 100 mL min^{-1} and $700 \text{ }^\circ\text{C}$ for 1 h, from which graphene A, B and C were obtained.

2.1.2. Graphene anode nitriding

After the GO paper was dried overnight, GO A was then nitrided inside a tube furnace. Two temperatures (800 and $950 \text{ }^\circ\text{C}$ for 2 h) were used with an NH_3 (anhydrous, Cryogenic Gases, Detroit, MI) atmosphere to reduce and, at the same time, to incorporate N on

Table 1
DLS sheet size and BET surface area measurements for the three different graphite sources and the resulting graphenes.

Sample	Graphite		Graphite oxide		Resulting graphene (powder)		Graphene anode (film)
	Source	Description	Surface area (BET)	Sheet size (DLS)	Sheet size (DLS)	Surface area (BET)	Surface area (BET)
A	Dixon Microfyne	44 μm Graphite Flakes	$3.07 \text{ m}^2 \text{ g}^{-1}$	$1266 \pm 33 \text{ nm}$	$238 \pm 2 \text{ nm}$	$172 \text{ m}^2 \text{ g}^{-1}$	$25.1 \text{ m}^2 \text{ g}^{-1}$
B	Asbury 230U	15 μm Graphite Flakes	$5.28 \text{ m}^2 \text{ g}^{-1}$	$542 \pm 14 \text{ nm}$	$160 \pm 4 \text{ nm}$	$380 \text{ m}^2 \text{ g}^{-1}$	$48.3 \text{ m}^2 \text{ g}^{-1}$
C	Asbury 2299	0.25–5 μm nano-Graphite powder	$342 \text{ m}^2 \text{ g}^{-1}$	$209 \pm 3 \text{ nm}$	$113 \pm 3 \text{ nm}$	$419 \text{ m}^2 \text{ g}^{-1}$	$58.2 \text{ m}^2 \text{ g}^{-1}$

Download English Version:

<https://daneshyari.com/en/article/1284303>

Download Persian Version:

<https://daneshyari.com/article/1284303>

[Daneshyari.com](https://daneshyari.com)