Electrochimica Acta 215 (2016) 126–141

Contents lists available at ScienceDirect

Electrochimica Acta

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

Hollow Silicon Nanospheres Encapsulated with a Thin Carbon Shell: An Electrochemical Study

Maziar Ashuri[a,b], Qianran He[a,b], Yuzi Liu[c], Kan Zhang[a,b], Satyanarayana Emani[a,b], Monica S. Sawicki[a,b], Jack S. Shamie[a,b], Leon L. Shaw[a,b,*]

[a] Department of Mechanical, Materials and Aerospace Engineering, Illinois Institute of Technology, Chicago, IL, USA
[b] Wanger Institute for Sustainable Energy Research (WISER), Illinois Institute of Technology, Chicago, IL, USA
[c] Center for Nanoscale Materials, Argonne National Laboratory, IL 60439, USA

ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form 20 July 2016
Accepted 12 August 2016
Available online 20 August 2016

Keywords:
Lithium-ion battery
Anode
Silicon
Hollow Si nanospheres
Sol-gel processing

ABSTRACT

In this study we have investigated the electrochemical properties of hollow silicon nanospheres encapsulated with a thin carbon shell, HSi@C, as a potential candidate for lithium-ion battery anodes. Hollow Si nanospheres are formed using a templating method which is followed by carbon coating *via* carbonization of a pyrrole precursor to form HSi@C. The synthesis conditions and the resulting structure of HSi@C have been studied in detail to obtain the target design of hollow Si nanospheres encapsulated with a carbon shell. The HSi@C obtained exhibits much better electrochemical cycle stability than both micro- and nano-size silicon anodes and deliver a stable specific capacity of 700 mA h g^{-1} after 100 cycles at a current density of 2 A g^{-1} and 800 mA h g^{-1} after 120 cycles at a current density of 1 A g^{-1}. The superior performance of HSi@C is attributed to the synergistic combination of the nanostructured material, the enhanced conductivity, and the presence of the central void space for Si expansion with little or no change in the volume of the entire HSi@C particle. This study is the first detailed investigation of the synthesis conditions to attain the desired structure of a hollow Si core with a conductive carbon shell. This study also offers guidelines to further enhance the specific capacity of HSi@C anodes in the future.

1. Introduction

Silicon is one of the most promising anode candidates for next-generation Li-ion batteries. This is due to its low voltage profile and high theoretical capacity (3590 mA h g^{-1} for $Li_{15}Si_4$ phase at room temperature), which is about ten times that of carbonaceous materials including graphite, pyrolytic carbon and meso-phase pitch (about 372 mA h g^{-1}) [1]. In addition, silicon is the second ample element in the earth's crust. Therefore, mass production of silicon with low cost is not an issue. However, practical application of silicon anodes is currently hindered by multiple challenges including the enormous volume change (~300%) during lithiation/delithiation processes, low intrinsic electrical conductivity, and instability of the solid electrolyte interphase (SEI) [2,3]. The large volume change can result in particle pulverization, loss of electrical contact with the conductive additive or current collector, and even peeling off from the current collector. The repeated volume expansion and shrinkage also lead to fracture and re-formation of the SEI layer around the particles, resulting in continuous consumption of the electrolyte, increased impedance, and capacity fading [2–8].

Significant efforts have been devoted to addressing the issues mentioned above. The strategies investigated include Si material design through nanostructures [9–13], porous structures [14–17], or nanocomposites [18–20], Si electrode design with combined nano- and micro-particles [21] or with 3D micro-channels [22], nanoporous SiO_x microparticles embedded in PANI-Ag layers [23], mesoporous SiO_x nanorods [24], addition of electrolyte additives [25], and use of novel binders [26,27]. Thanks to the worldwide efforts, rapid advancements have been made in the properties and performance of Si anodes [28]. Examples of such breakthroughs include exceptional specific and volumetric capacities at 1160 mA h g^{-1} and 1270 mA h cm^{-3}, respectively, after 1000 cycles at the C/2 rate accomplished through a pomegranate-inspired nanoscale design [13], high specific and volumetric capacities at 1600 mA h g^{-1} and 1088 mA h cm^{-3}, respectively, after 150 cycles at 400 mA g^{-1} achieved *via* a

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[*] Corresponding author at: Department of Mechanical, Materials and Aerospace Engineering, Illinois Institute of Technology, Chicago, IL, USA.
E-mail address: lshaw2@iit.edu (L.L. Shaw).

http://dx.doi.org/10.1016/j.electacta.2016.08.059

micro-sized porous Si/C material [16], and a specific capacity of 1450 and 1230 mA h g^{-1} after 100 cycles at 100 and 500 mA g^{-1}, respectively, obtained *via* a low cost, double-shelled Si@SiO_x@C core-shell structure [29].

Among various methods for Si material design, Si particle-based structures have attracted significant attention. Examples of Si particle-based structures include solid nanoparticles [3,29], solid core-shell structures [30–33] or core double-shell structures [34], and yolk-shell structures [10,11,35–38]. Lately, Chen, et al. [39] have investigated another type of structure which is composed of a hollow Si core encapsulated by a conductive shell (termed as hollow core-shell structures hereafter). Their study shows that the hollow Si core encapsulated with an Ag shell can deliver outstanding performance (i.e., ~2,900 mA h g^{-1} after 100 cycles at the current density of 0.5 A g^{-1}) because of the synergistic combination of the nanostructured material, the formation of adequate void inside for volume expansion, and the enhanced conductivity. In contrast, the hollow Si core encapsulated with a carbon shell exhibits less optimized performance than the hollow Si core encapsulated with an Ag shell, which is most likely due to the higher electrical conductivity of Ag than that of carbon [39]. In spite of the less optimized performance, the hollow Si core encapsulated with a carbon shell deserves additional investigation because carbon is more stable than Ag at the anodic condition. As reported in Ref. [39], the Ag shell starts to degrade after 100 cycles, indicating that the long-term cycle stability of the hollow Si core encapsulated with an Ag shell is questionable. In addition, a carbon shell can be deposited through a wide range of techniques such as chemical vapor deposition (CVD), carbonization of polymers, and wet chemistry methods with different precursors (sucrose, glucose, polydopamine, pyrrole, etc.) [3,30,31,37,40–42], making the hollow Si core encapsulated with a carbon shell attractive from the viewpoints of both low cost synthesis and long-term cycle stability.

In this study, we have investigated synthesis and properties of the hollow Si core encapsulated with a carbon shell (HSi@C) by forming hollow Si spheres first, followed by carbon coating *via* carbonization of a pyrrole precursor. The hollow Si spheres are formed using a templating method, while the carbon coating formation is a facile carbonization treatment that does not require expensive equipment such as chemical vapor deposition (CVD) reactors. HSi@C anodes exhibit much better electrochemical cycle stability than both micro- and nano-size silicon anodes and deliver a stable specific capacity of 700 mA h g^{-1} after 100 cycles at a current density of 2 A g^{-1} and 800 mA h g^{-1} after 120 cycles at a current density of 1 A g^{-1}. These properties are better than those obtained from many other Si material designs [36,41,43–48]. With the aid of a range of advanced analytical methods, the superior performance of HSi@C has been attributed to the unique engineered design of HSi@C nanospheres, i.e., a conductive carbon shell for enhanced conductivity with the central void space for Si expansion. The structural defects in HSi@C have also been identified to provide guidelines for further improvement of HSi@C in the near future.

2. Experimental Details

2.1. Synthesis of carbon-coated hollow silicon spheres

The synthesis steps of this study are shown schematically in Fig. 1. The synthesis started with polystyrene (PS) nanoparticles as templating agent onto which SiO_2 was deposited *via* a sol-gel reaction (Fig. 1a and b) to form SiO_2-coated PS nanoparticles (PS@SiO_2). The PS core was then removed to generate hollow SiO_2 spheres (HSiO_2) which were converted to hollow Si spheres (HSi) *via* magnesiothermic and hydrogen reductions (Fig. 1c and d). Finally, HSi was encapsulated with a thin carbon shell to form hollow silicon nanospheres encapsulated with a thin carbon layer (HSi@C, Fig. 1e). The synthesis details are described below.

Commercial positively charged polystyrene (PS) nanoparticles suspension (with the diameter of PS nanoparticles at ~200 nm) was purchased from Sciventions Inc. and used as templating agent (Fig. 1a). The suspension was dispersed in a mixture of deionized water (16 mL) and ethanol (10 mL). Then, cetyltrimethylammonium bromide (CTAB, 10 mg) was added to the mixture and let the mixture stir for 10 min. This was followed by addition of concentrated ammonia aqueous solution (5 wt. %, 0.0428 mL) and then the addition of 0.48 mL of tetraethyl orthosilicate (TEOS) as silica precursor. The reacting sol-gel solution was stirred at room temperature for 3 h to form PS@SiO_2 nanoparticles (Fig. 1b). The suspension was then centrifuged and washed with ethanol three times. The precipitates were collected and dried at room temperature for two days. The collected PS@SiO_2 nanospheres were calcined inside a tubular furnace at 600 °C for 6 h to burn out the PS core (Fig. 1c). The hollow silica spheres obtained were subsequently mixed with magnesium hydride (MgH_2) powder and placed in a tantalum boat crucible inside an argon-filled glovebox. MgH_2 powder was used because its particle size was finer than Mg powder and thus resulted in better mixing with PS@SiO_2 nanospheres. The loaded crucible was then transferred to a homemade Swagelok® pipe reactor which was put into a tubular furnace and subject to heating up to 700 °C for 5 h. This step resulted in reduction of hollow SiO_2 spheres to hollow Si spheres by H_2 and Mg (Fig. 1d). Next, the reduced HSi nanospheres were dispersed in 1 M hydrochloric acid (HCl) and sonicated for 3 h or 6 h to dissolve residuals of Mg and also MgO compound formed during reduction. The nanospheres were washed with pure ethanol and deionized water 3 times. Eventually, HSi nanospheres were mixed with pyrrole (in 8:1 to 11:1 molar ratio) in a quartz crucible and then loaded into a stainless steel autoclave inside an argon-filled glove

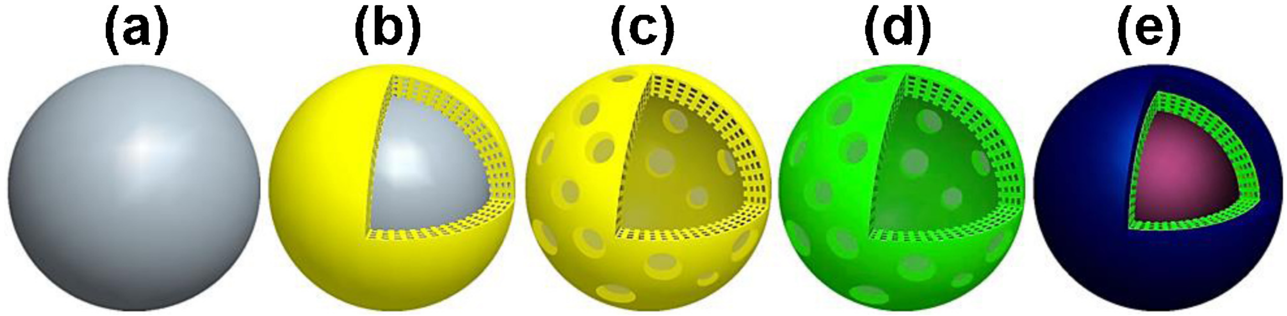

Fig. 1. Schematic of synthesis steps: (a) PS nanoparticles, (b) PS@SiO_2, (c) HSiO_2, (d) HSi, and (e) HSi@C. See the text for details.