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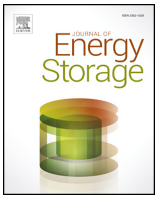

Binder and conductive additive free silicon electrode architectures for advanced lithium-ion batteries

Sarode Krishna Kumar, Rini Choudhury, Surendra K. Martha*

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, 502285, Telengana, India

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ABSTRACT

This manuscript presents binder and conducting additive free Silicon nanoparticles (Si-NPs) as anodes for lithium-ion batteries. The Si-NPs are pressure embed onto copper foil current collector without using any organic binder or conductive carbon additive. It presents physical and structural studies by XRD, SEM, Raman, TEM and electrochemical performance of Si-NPs by electrochemical impedance spectroscopy and galvanostatic charge-discharge cycling. Binder-free Si-NP electrodes exhibit an initial reversible capacity of 950 mAh g^{-1} at C/10 rate and more than 650 mAh g^{-1} during 500 cycles at C/2 rate. The electrodes shows excellent rate capability (800 mAh g^{-1} at 5 C rate) and cycling stability, because of available free space for volume change during cycling of silicon NPs without pulverization. The binder-free anode fabrication enables Si-NPs to obtain the real capacity of silicon without any interference of capacity contribution from composite materials.

1. Introduction

Silicon is considered as one of the most attractive anode materials for advanced Lithium-ion batteries (LIBs). While the commonly used graphite anodes have a specific capacity of only 372 mAh g^{-1}, silicon can alloy up to 4.4 Li atoms at room temperature, delivering capacity close to 4200 mAh g^{-1} [1–4] which is the highest theoretical capacity of all known anode material available today. In addition to the capacity, it has a lithiation potential close to that of graphite (i.e. 0.4 V vs. Li/Li^+) [1–4] and is non-toxic, and high abundance in the earth's crust. In spite of these advantages, there are certain fundamental challenges to the use of silicon as a viable anode material for LIBs. These include (i) large volume expansion/contraction (~400%) during lithium insertion/extraction induces large stresses, leading to pulverization of Si which in turn causes loss of electrical contact and eventually leads to capacity fade [2–5], (ii) the lack of a mechanistic understanding of the nature of solid electrolyte interphase (SEI) formation on the silicon surface and its stability during the repeated expansion and contraction during cycling [2–4,6].

It has been shown that nanostructured silicon anodes circumvent volume modification as they can accommodate large strain without pulverization, provide good electronic contact and conduction, and display short lithium insertion distances [3–5,7–22]. A variety of silicon nanostructures [3,4,7–22] and silicon/carbon composites [12–20], 3D electrode architectures [3,22], core shell structures [14,17] have been investigated to overcome the problems associated with volume expansion, capacity fade and low cycling stability. There are many reports to overcome the issues of pulverization due to volume change. Recently, Si-nanoparticles (NPs) showed the stable charge capacity of 2000 mAh g^{-1} by introducing the carbon-silicon core-shell nanowires for high power and long cycle life LIBs [17]. 2D amorphous silicon nanowalls which retains the advantages of 1D silicon nanotubes shown to have improved initial coulombic efficiency and stable capacity of 2100 mAh g^{-1} at C/5 rate [16]. Si@C@Void@C nanohybrids shows an enhanced reversible capacity of 1366 mAh g^{-1} after 50 cycles at 500 mA g^{-1} by developing core-shell yolk-shell structure [17]. Hollow core-shell structured silicon@carbon nanoparticles embedded in carbon nanofibers attained high reversible capacity of 1020.7 mAh g^{-1} after 100 cycles at a current density of 0.2 A g^{-1} [18].

However, the nano-size interface between the nanostructured active material and the current collector results in a high electrical contact resistance, which also impairs the efficiency of electron transport. In addition, the small contact area undergoes a high shear stress when silicon swells during lithiation, potentially causing separation of active material from the substrate [5]. Like this there are many ways of making silicon with different shape and sizes or morphologies which involves many complex steps to circumvent the volume change during cycling. Moreover, there is also a challenge of fabricating the silicon anode with free expansion of space for Silicon. i.e., proper attaching of the different silicon morphologies with the copper current collector for stable electrochemical cycling.

In this work, we present a simple method of electrode fabrication

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* Corresponding author.
E-mail address: martha@iith.ac.in (S.K. Martha).

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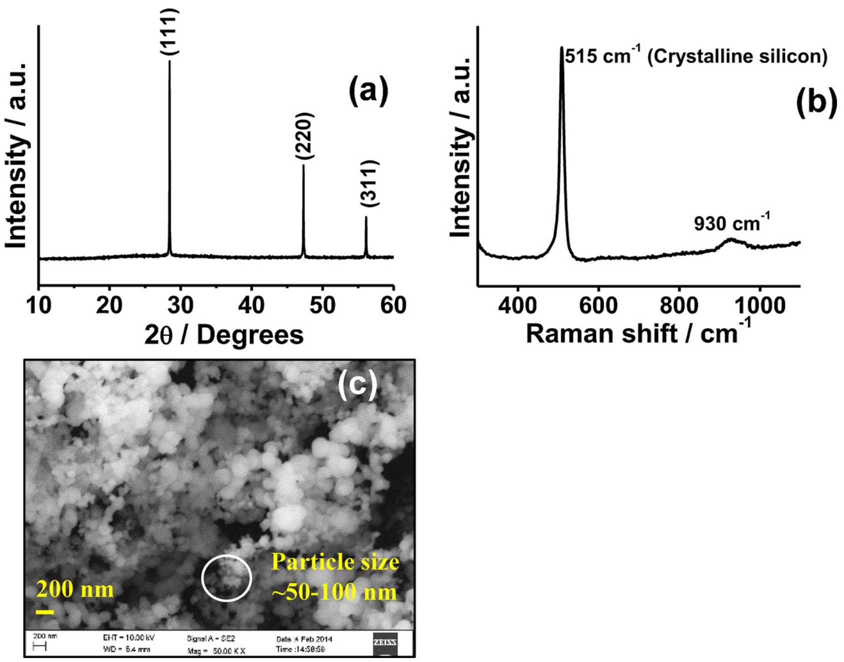

Fig. 1. (a) X-ray diffraction pattern of as-synthesized Si-NPs by magnesiothermic reduction from fumed silica; (b) Raman spectra of the as-synthesized Si-NPs; (c) SEM image of the as-synthesized Si-NPs indicating few particle sizes.

where we use spherical silicon NPs synthesized by magnesiothermic reduction [11] from fumed silica. The as-synthesized silicon NPs were manually pressed onto copper foil as the current collector, without addition of any conductive carbon or organic binder. The goal is to ensure proper attachment of the active material on to the current collector by pressure-embedding the Si-NPs, in order to eliminate the interface between the two as far as possible. This in turn will minimize the contact resistance, facilitating electron transport and thus improving cycling capability. In addition, less particle loading, uniform distribution of Si-NPs will ensure that all the active material which has been pressed onto the current collector takes part in the electrochemical reaction, further enhancing electrochemical performance. This is the simplest and most cost effective method of electrode fabrication compared to other methods.

2. Experimental

Silicon NPs are synthesized by magnesiothermic reduction [11] where the stoichiometric amounts of fumed silica and magnesium powder (1:2 mol ratio) are mixed well in a mortar pestle for 1 h h followed by annealing at 700 °C for 2 h under argon gas. The silicon NPs are obtained by removing the MgO and Mg_2Si by treating the obtained product with 1N HCl solution. The Powder XRD measurements were performed by using a Panalytical X'Pert Pro diffractometer (The Netherlands) (reflection θ − θ geometry, Cu Kα radiation, receiving slit of 0.2 mm, scintillation counter, 30 mA, 40 KV). The diffraction data were collected at 0.02 step widths over a 2θ range from 10 to 60^0. The surface morphology of the composite powders were further measured by scanning electron microscope (Carle Zeiss SUPRA™ 40 Field Emission Scanning Electron Microscope) and transmission electron microscopy (JEOL-2100 plus transmission electron microscope) and compositions by energy dispersive X-ray microanalysis (EDAX) systems from Oxford instruments. It was further characterized by Raman spectroscopy using a micro Raman spectrometer HR800 (Jobin Yovn Horiba, France), with He-Ne laser (excitation line 632.8 nm) and a microscope objective (50 ×, Olympus Mplan, 0.4 mm working, numerical aperture 0.75 in back scattering configuration).

Electrodes were prepared manually by pressure embedding the as synthesized Si-NPs onto copper foil current collector for 30 mins, without using any additional conductive carbon or organic binder. The silicon pressure embedded electrodes on to copper foil were then placed under vacuum oven at 90 °C for overnight to remove moisture followed by punching into 1 cm^2 circular disc. For comparison, composite electrodes were prepared using 50 wt.% active material (Si NPs), high surface area carbon, ACS 2500 (40 wt.%.) (China Steel Chemical Corporation, Taiwan) and binder 10 wt.% polyvinylidene fluoride binder (Kynar, Japan), dissolved in *N*-methyl-2-pyrrolidone (Sigma Aldrich) were mixed in a planetary ball mill mixture (Gelon, China) for 1 h to form slurry. This slurry was then coated onto copper foil using the doctor-blade technique. The as-prepared conventional Si composite electrode was then dried at 90 °C under vacuum for overnight, punched and weighed and used as anodes.

The electrochemical performance of the as-prepared Si on Cu and composite electrodes was evaluated in two-electrode Swagelok type cells with pure lithium foil (Alfa Aesar) as the counter electrode, Si electrode sandwiched between 2 polyethylene-polypropylene- polyethylene membrane separators (Celgard Inc.). The electrolyte comprised 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) (Merck, India). The cells were assembled in a glove box filled with pure argon gas (MBraun, Germany). Galvanostatic charge–discharge cycling was carried out using a multichannel battery tester (Arbin BT2000 – Battery Test Equipment, USA) within the operating voltage range of 1.2–0.05 V. The impedance measurements of these composite electrodes and pressure embodied Si electrodes were measured by using Solartron cell test system consists of 1470E multi-channel potentiostats and multiple 1455A series frequency response analyzers (FRAs) (driven by Corrware and ZPlot software from Scribner Associates). The impedance measurements were carried out in a frequency range between 1 MHz and 10 mHz before and after 1st cycles and 60 and 500 cycles at 1.2 V for composite and pressure embodied Si electrodes, respectively. Postmortem TEM analyses were conducted on cycled Si anodes. The powdery Si-NPs were separated from Cu current collector by sonication, followed by washing several times with pure DMC solvent, dried under vacuum and used for analysis.