



Dependence of thermal stability of lithiated Si on particle size



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HIGHLIGHTS

- At fully lithiated silicon, nanometer particles exhibited larger exothermic heat by DSC.
- The rate of release heat is related to the state of charge for different particles.
- Surface components of silicon are detected by XPS at different temperatures.
- SEI decomposes below 200 °C, and rapid reaction of Li with electrolyte leads thermal changes above 200 °C.

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ABSTRACT

Thermal properties of the component materials are key issues in lithium ion batteries (LIBs). Si-based anodes are one of the most promising materials, but its thermal evolution have received much less attention than its electrochemical performance. In this article, the thermal behavior of various of Si material has been studied by differential scanning calorimetry (DSC). Three kinds of Si-particles, ranging from nano-to micro-sizes was subject to thermal analysis. It has been found that the thermal stability increases with the rise in particle-size. For the nanoparticles of 20 nm, both characteristic peaks of A and B regions in the heating process are stronger than the large-diameter particles. For three kinds of Si particles, the starting temperature of thermal reaction demonstrates a similar trend, gradually becoming lower with the increasing of the lithiation extent. At last, the *ex situ* XPS has also been conducted to explore the causes of surface state after temperature elevation. In A region, the heating decomposition of SEI with electrolyte, mainly consisting of a variety of esterification compounds, produces high content of lithium carbonate below 180 °C. When lithium in the inner phase of Si particles loses the protection of SEI film, the severe exothermic reaction occurred between lithium and the solvent species.

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1. Introduction

Lithium ion batteries (LIBs) have become one of the important storage energy technologies, especially in portable devices, electric vehicles, and many other fields [1–3]. However, the safety issue of LIBs is one of the potential hazards for society and users. In particular, it is important to understand the exothermic reaction at

elevated temperature, so-called thermal abuse in safety test. The thermal abuse of material in LIBs has been widely studied in many publications [4,5]. The electrode material can undergo a series of reactions during the heating process, which necessitate a detailed investigation. When LIBs are heated to a temperature about 150 °C, some side-reactions such as decomposition reactions gradually occurs at the solid electrolyte interface (SEI) covering anode (mainly graphite) surface. This in turn will lead to further temperature rise and the generation of various gases (most of gases may come from the decomposition of SEI with electrolyte solutions). Above 200 °C, the lithium intercalation in graphite liberates much more heat flow, and become even more severe, which is likely to

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trigger thermal decomposition of cathode material and thermal runaway of the complete LIBs [6–8]. In the past decades, many researchers have paid attention to these concerns, and most of them mainly focused on the traditional anode material of graphite [9–12]. In recent years, silicon anode is gradually introduced into LIBs; however, their thermal safety has been hardly studied [13,14].

Currently, Si-based anode is one of the hot points in battery material. The excellent specific capacities have received extensive attention; however, its huge volume effect hinders the cycling performance and applications. In most studies, various nanostructures such as nanowires, nanoparticles, and nano-films, have been introduced into Si anodes to ameliorate the negative effect of drastic volume change at high lithiation levels [15–18]. However, the nanostructure particle always has a high specific surface area, which induces instability at the interface with electrolyte solutions [19]. In particular, this problem has changed to a serious safety issue at elevated temperature or thermal abuse.

Herein, we report a detailed investigation on the thermal stability of Si-based material at elevated temperature by using three kinds of particles, such as 20 nm, 200 nm, 1.5 μm . The Si electrodes with different lithiation extents were placed in a sealed pan to study the differential scanning calorimetry (DSC) curves in the temperature range from 50 to 350 $^{\circ}\text{C}$. By monitoring the heat flow during temperature rise, the thermal stability of electrodes was investigated at a certain state of charge (SOC). At the same time, the *ex situ* X-ray photoelectron spectroscopy (XPS) was detected on heated Si electrodes, and the causes of thermal reaction at different heat-treatment was analyzed.

2. Experimental

Si samples with different particle sizes, such as SP1 (20 nm), SP2 (200 nm), SP3 (1.5 μm), were used in DSC and XPS measurement. The morphologies of Si particles were detected by scanning

electron microscopy (SEM) as shown in Fig. 1 a, b, and c. Si-based slurry were prepared by mixing 80 wt% Si-particles (milled-particle or commercial), 10 wt% Super-P (Timcal, Switzerland) and 12 wt% polyvinylidene fluoride (PVDF, HSV-900, Arkema, France) in the solvent of *N*-methyl pyrrolidinone (50 wt%, NMP, Aladdin, China). This slurry was cast onto a copper foil by semi-automatic coating machine (scraper height 100 μm). The Si electrodes were dried at 110 $^{\circ}\text{C}$ under vacuum for 6 h. The mass loading of three electrodes were approximately 0.8 mg cm^{-2} (SP1), 3.1 mg cm^{-2} (SP2), 10.6 mg cm^{-2} (SP3), respectively.

The Li/Si coin cells (CR 2032) were assembled in a glove box filled with dry Ar atmosphere. Within each cell, a sliced Si-electrode and a Li-plate were separated by a piece of separator (polyethylene, 22 μm , Cergard 2400), which was soaked with the electrolyte solution (about 100 μL) of 1 M LiPF_6 dissolved in the mixed solvents of ethylene carbonate and ethyl methyl carbonate (EC-EMC, weight ratio 3:7). The lithiation of Si electrodes was accomplished by discharging Li/Si coin cells to the voltages of 240, 170, 50 and 5 mV, respectively.

A constant current of 0.1 C (about 0.25, 1, 4 mA cm^{-2} for SP1, SP2, SP3 samples) was applied. Cells with different SOC were carefully disassembled in the glove box (dew point ≤ -70 $^{\circ}\text{C}$). Then a recovered Si electrode was placed into a polypropylene (PP) pipe (5 mL) filled with dimethyl carbonate (DMC) (about 2 mL), and the pipe was shaken about 3 min by hand. After resting 15 min, the electrodes were taken out from the pipe and the DMC solvent was wiped out by filter paper to remove the free-electrolyte. Then, Si electrodes were further dried in vacuum environment. At last, a certain amount (about 2 mg) of scraped-off electrode material weighed and sealed in DSC ceramics pans with electrolyte, which the amount of electrolyte was 50 wt% of that active material. All the sample preparation was performed in a glove box. DSC measurements were operated by the DSC instrument (SETARAM, DSC131, Evo) at a heating rate of 2 $^{\circ}\text{C min}^{-1}$ within a temperature range

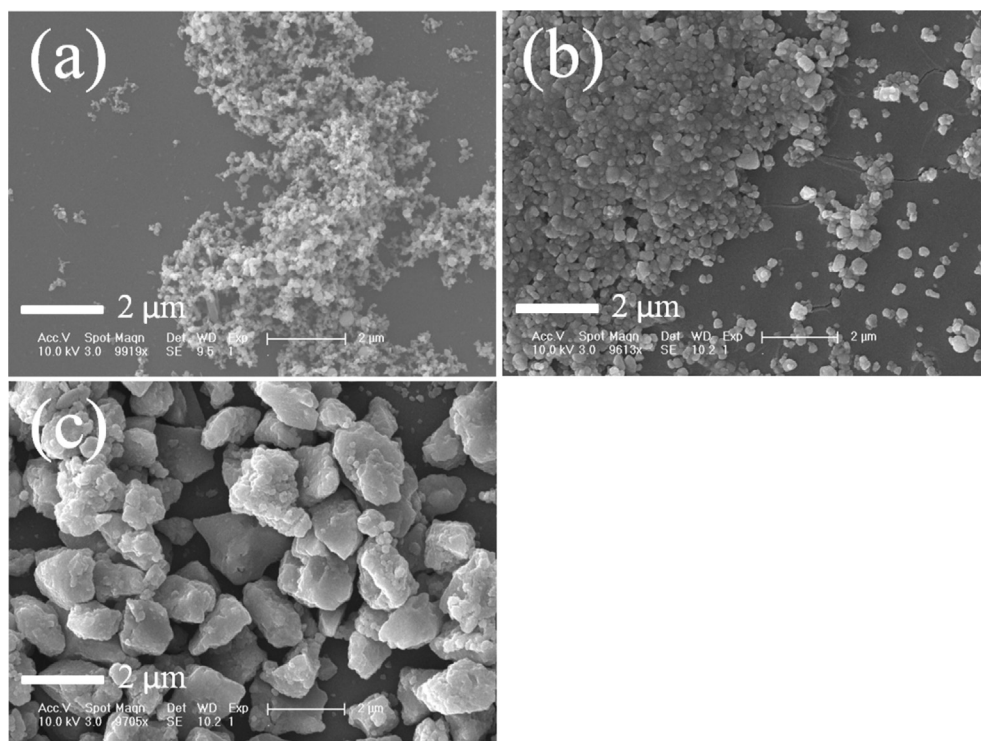


Fig. 1. Scanning electron microscopy (SEM) images of Si samples: (a) SP1: nanometer Si-particle (20 nm), (b) SP2: nanometer Si-particle (200 nm), (c) SP3: micrometer Si-particle (1.5 μm).

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