



# Recycled crystalline micro-sized silicon particles modified by pyrolytic coatings using poly(ether ether ketone) precursor for stable lithium ion battery anodes

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## ABSTRACT

Crystalline micro-sized Si wafer sawing chips recycled from the waste slurry are modified to be practical anode materials by designated pyrolytic coatings using Poly(ether ether ketone) (PEEK) as the precursor. Si-C composite particles are obtained at different pyrolysis temperatures (500–800 °C), covering different stages of polymer degradation in PEEK. The Si-C anodes obtained at a suitable pyrolysis temperature exhibit an initial capacity greater than 2000 mAhg<sup>-1</sup> and less than 10% of initial irreversible capacity at 0.1 C. The Si-C anode exhibits a reversible capacity of 960 mAhg<sup>-1</sup> with capacity retention of ~90% over 50 cycles at 1 C. The designated pyrolytic coating provides a buffer layer, which serves as a conductive pathway as well as a durable surface cap to accommodate the huge volume change during lithiation and de-lithiation of Si. These originally unusable Si particles are modified into practical Si-C composites with enhanced capacity and cycling stability.

## 1. Introduction

Lithium-ion batteries (LIBs) are commonly used power sources for portable electronics and electric vehicles [1–3]. The conventional anode material in LIBs is graphite, which possesses a theoretical capacity of 372 mAhg<sup>-1</sup> [3]. For high energy density LIBs, Si is one of the alternative anode materials under intensive study, due to the high theoretical capacity of 4200 mAhg<sup>-1</sup> [4]. It however suffers from low cycling stability, which is attributed to the large volume change of 400% during charge-discharge cycles. The stress accumulated from the volume change induces cracks and deteriorates the Si anodes. The cracked Si particles lose electric contacts to the conductive additives and current collectors, resulting in rapid capacity fading [5,6]. In addition, the cracking also results in the growth of secondary solid electrolyte interface (SEI) layers, which further consume the electrolyte and reduce the reversible capacity.

In order to address the above mentioned issues, many approaches have been reported, notably the use of nano sized/structured [7,8] and carbon coated [9] Si particles. It is generally agreed that the nano sized/structured Si can shorten the Li<sup>+</sup> diffusion path and relieve the stress induced by the volume change. The carbon coatings on Si are believed to mitigate and accommodate the large volume expansion, as well as increase the electric contacts among particles, assisting the

charge transfer. Carbon coatings can be obtained by pyrolysis of various carbon containing precursors such as glucose [10] and polyvinylidene fluoride [11] (PVDF). For micro-sized or polycrystalline Si powders, the well crystallized structures are even more vulnerable to the volume change [4–11]. The specially designed nano structures or carbon coatings are generally required to avoid the notable capacity fading during extended cycles. It was reported that well crystallized Si, such as the Si wafers, can be modified to be used as an anode material for lithium ion batteries [12], where the Si wafer was etched to produce micro-porous Si, followed by pyrolysis of polyacrylonitrile (PAN) to form a conductive network. More recently, Zhang et al. [13] used micro-sized polycrystalline Si particles as the starting material, and fabricated nano-porous Si with metal induced etching, followed by pyrolysis of PAN. However, the fabrication of nano structured Si is often expensive and time consuming. As a consequence, a widely accepted commercial product has yet to be developed.

In the present paper, cost effective and abundant Si powders obtained from the waste slurries of Si wafer sawing process have been used and modified. Si particles recycled from the sawing waste are of low cost but well-crystallized and micro-sized, which are generally vulnerable to volume expansion induced cracking. It is demonstrated in this study by using poly(ether ether ketone) (PEEK) as the precursor, and by properly designing the pyrolysis temperatures, the pyrolytic

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carbon coatings are able to accommodate the volume change and the subsequent stress evolution. The well crystallized micro-sized Si powders recycled from sawing waste have therefore been modified to be a low-cost and easily scalable Si-C composite anode material with improved capacity and cycling stability.

## 2. Material and methods

The precursor used here is the PEEK polymer, which has to be sulfonated to increase the solubility in organic solvents. However, the molecular structure of PEEK is composed of many aromatic rings. Those aromatic structures start to form fluorenones in elevated temperatures and readily carbonize or even graphitize. It makes the PEEK polymer a suitable precursor to form carbon. To prepare the precursor solution, commercially available PEEK powder was purchased from Victrex plc. The PEEK powder (5 g) was dissolved in 98% sulfuric acid (100 mL), followed by continuous stirring at 50 °C for 12 h. After full dissolution of the PEEK powder, the solution was poured into cold water (5 °C) and the precipitates were removed from the cold water. The obtained precipitates were then washed by deionized water to remove the residual sulfuric acid until the pH value reached 7. The precipitates were then dried at 120 °C for 48 h. The obtained polymer was found to be 65% sulfonated, as estimated by the titration method [14]. A proper amount of the dried precipitates (5 g) was then added in 100 mL of dimethyl sulfoxide (DMSO), and the mixture was stirred at room temperature until a fully dissolved precursor solution was obtained.

The Si particles (99.9%) used in this study were provided by GET Green Energy Corp. Ltd. Taiwan, which were recycled from the waste slurry of the cutting/sawing processes of the crystalline Si wafers. The Si particles were added into the sulfonated PEEK solution (in DMSO), and the mixture was blended in a mixer (Chemist, MH-4000D) at 1200 rpm for 1 h. The weight ratio of the sulfonated PEEK and the Si particles is controlled at 1:9. The obtained slurry was dried and annealed in Ar atmosphere for 1 h for pyrolysis and carbonization of the sulfonated PEEK. Si-C composites with carbonization temperatures of 500 °C, 600 °C, 700 °C and 800 °C were prepared and denoted as Si500, Si600, Si700 and Si800. The slurry of the anode electrodes was prepared by mixing 80 wt% of the obtained Si-C composite powders with 10 wt% of carbon black and 10 wt% of PVDF binder in *n*-methyl-2-pyrrolidone (NMP) solvent. The slurry was then coated on battery grade Cu foils using a doctor's blade coater. The thickness of the electrode is 75  $\mu\text{m}$ . The coated electrodes were dried at 120 °C for 12 h.

The sizes of Si particles were measured in Get-green energy Corp. by using a size distribution analyzer, and particles of larger sizes ( $> 7 \mu\text{m}$ ) were sieved. The crystal structure of the Si powder was characterized by powder X-ray diffraction (XRD, Bruker D8SSS). Thermogravimetric analysis (TGA) was carried out using a thermal analysis station (TA TGA2950) under nitrogen flow. Cold field-emission scanning electron microscope (SEM, HITACHI S-4800), and transmission electron microscope (TEM, Joel JEM-2100) equipped with an energy dispersive X-ray spectroscope (EDX) were used to characterize the morphologies and elemental contents of the Si-C particles and anode electrodes. Raman spectra of the Si-C particles were measured by a micro Raman spectroscope (ProtrusTech AutoRam) using a diode-pumped solid state laser (wavelength = 532 nm).

The prepared electrodes were punched into 1.33  $\text{cm}^2$  discs and assembled in coin cells (CR2032) with polypropylene separators (Celgard 2400) and lithium metal foils (as counter and reference electrodes). The electrolyte solution was 1 M  $\text{LiPF}_6$  in ethyl carbonate/ethyl methyl carbonate (EC/EMC volume ratio of 1:2). The cells were characterized using a galvanostatic electrochemical station (Jiehnan 5500). Charge/discharge measurements were conducted at 0.1 C and 1 C rates within a voltage range of 0.01–1.50 V (vs.  $\text{Li}/\text{Li}^+$ ). Cyclic voltammetry (CV) curves were measured with a scan rate of 0.2  $\text{mVs}^{-1}$  within a voltage window of 0.05–1.50 V (vs.  $\text{Li}/\text{Li}^+$ ). The masses of the Si-C composite electrodes were weighted by a microbalance and used for calculating

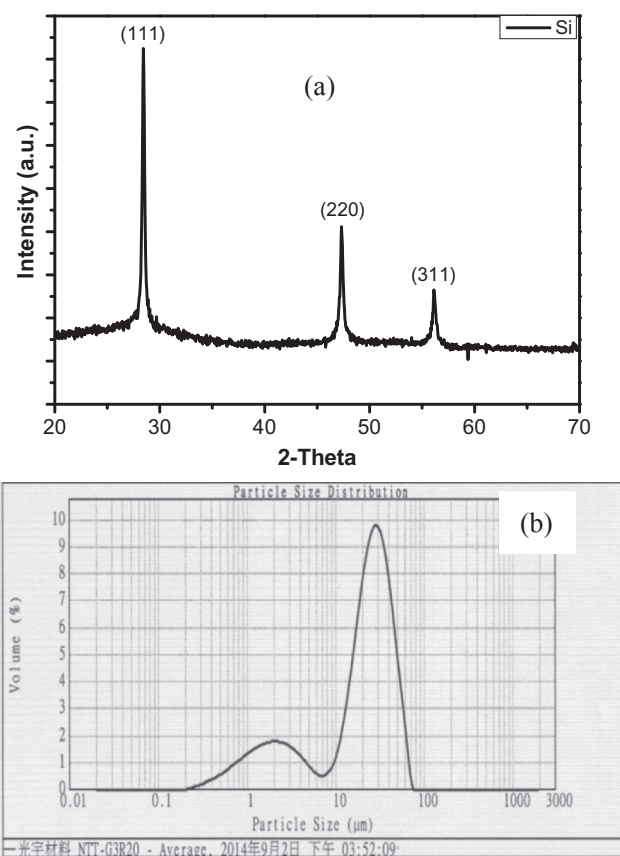


Fig. 1. (a) XRD diffraction patterns of the as received Si particles, showing well crystallized pure Si phase, and (b) size distribution of the original Si particles, where the larger particles ( $> 7 \mu\text{m}$ ) were sieved in the recycle processes of Get-green energy Corp. Ltd.

the specific capacity. The loading mass of the active materials is  $0.9 \text{ mgcm}^{-2}$ . Electrochemical impedance spectra (EIS) measurements were carried out on a Hioki 3522 analyzer over the frequency range of  $10^5$ – $10^{-2}$  Hz with an amplitude of 20 mV.

## 3. Results and discussion

The XRD diffraction measurement of the as received Si powder is shown in Fig. 1(a). Sharp diffraction peaks of Si (1 1 1), (2 2 0) and (3 1 1) are recorded, indicating the well crystalline nature of the Si powder recycled from the wafer cutting waste. No second phases are detected in the XRD measurement. Fig. 1(b) shows the size distribution of the as-recycled Si particles, where two distribution groups are recorded. The larger group was sieved in Get-green energy Corp., and only the smaller group was used in this study. As shown in Fig. 1(b), the sizes in the small-size distribution group vary from 200 nm to 7  $\mu\text{m}$ , and the predominant size is 2  $\mu\text{m}$ . Fig. 2(a) shows the SEM micrograph of the as-received Si powder. The Si particles are of flake shape, which are the typical shape and size of Si wafer cutting chips. The sizes of the Si particles vary from 200 nm to 5  $\mu\text{m}$ , with the predominant size of around 2  $\mu\text{m}$ , which confirms the size distribution in Fig. 1(b). An individual Si-C composite particle after pyrolysis of sulfonated PEEK at selected temperature (700 °C) is examined under TEM (Fig. 2(b)), where a flake-shaped dark particle is wrapped with gray coating. The coating is not conformal, such that some parts of the particle are exposed. Since the Si particles are cutting chips, the surface is too coarse for detailed observation of the pyrolytic carbon coating. Instead, an EDX spot analysis was taken at the dark and gray regions. The arrows in Fig. 2(b) indicate two spots for EDX analysis, and it is revealed that the dark spot is a part of one Si particle with 90.74 wt% of Si and 9.26 wt%

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