

Composite Li-Ion Anodes from Recycled Silicon

Wanli Xu

Electrochemical Materials, LLC,
8000 Innovation Park Drive, Baton Rouge, LA 70820
wanli.xu@electro-mat.com

ABSTRACT

In this work, we describe a method to recycle silicon from silicon waste for use in a lithium ion battery. Through this procedure, silicon waste from semiconductor manufacturing can be recovered and treated to produce surface modified silicon nanoparticles for use as anode material for lithium ion rechargeable batteries. Specific anode capacity can be maintained at 650 mAh/g for over 50 cycles at 70% DoD.

Keywords: lithium ion battery, silicon, energy storage, surface modification

1 INTRODUCTION

Rechargeable lithium batteries are commonly used in portable electronic devices such as cell phones, tablets and laptop computers. They are also used in electric vehicles. Conventional batteries are made using spinel cathodes and graphite anodes. These batteries are limited to a capacity of approximately $100 \text{ mAh}\cdot\text{g}^{-1}$ [1]. There is considerable interest in new electrode materials that would increase the capacity of lithium ion batteries.

Silicon has become a promising candidate to replace graphite as the anode material for rechargeable lithium ion batteries. Silicon has a theoretical capacity for lithium storage of $4200 \text{ mAh}\cdot\text{g}^{-1}$, which is over ten times higher than that of conventional graphite material. Despite the extremely high specific capacity, silicon as an anode material shows high volumetric expansion of over 300% when fully charged with lithium[2]. The volumetric expansion will result in cracking and pulverization of silicon, leading to poor cycle performance for bulky silicon anodes. Recent research on nano-structured silicon (including silicon nanoparticles, nanowires, nanotubes, complex 3-D structures, etc.) has demonstrated great potential in achieving both high capacity and extensive cycle life for silicon anodes in lithium batteries[3-11]. An important concern centers on the composition, size and shape of silicon that could be used to produce a high-capacity silicon anode.

There are many methods to create silicon anodes using various sources of silicon. Silicon anodes may be made using solely silicon as the active material. Silicon may also be combined with other active materials, such as graphite, to form composite anodes. Silicon-only anode materials,

such as nanowires, nanofilms or other nanostructures, are typically created by a vapor deposition process; for example, chemical vapor deposition (CVD) using silane precursors such as SiH_4 [5, 10, 12]. Silicon in composite anodes typically originates from growth methods such as CVD, solution growth, or from subtractive methods such as laser ablation, etching, or mechanical attrition. In general, the aforementioned methods of producing silicon are expensive and the resulting materials may not be ideally suited for use in anodes due to their size, shape, purity, composition, or surface chemistry. For example, nano-silicon produced via CVD usually shows high purity and controllable morphology; however, high cost, low yield, and toxic precursors prevent commercialization from CVD process. Silicon nanowires generated via patterned etching involves costly photolithography and electrochemical etching in hydrofluoric acid. Metal-assisted electroless etching in hydrofluoric acid to produce silicon nanowires is scalable and capable of mass fabrication; however, the diameter of silicon nanowires is not facilely controllable in this electroless etching process.

Currently, about 80% of the initial metallurgical-grade silicon material is wasted during the process of making silicon solar cells or wafers[13]. After a silicon ingot is grown, it is sliced into wafers. Sawing with multiple wiresaws is now the preferred method used to slice silicon ingots. Wiresaw technology can produce wafers as thin as 200 micrometer; however, a layer of silicon about 250-280 micrometers thick is typically lost per wafer. Depending on wafer thickness, kerf loss represents from 25% to 50% of the silicon ingot material [13]. Likewise, waste particles are generated when the wafers are lapped or polished to their final thickness. Lapping and polishing operations remove an additional 5 to 30% of the final product wafer. The waste is difficult to recycle due to the presence of solvents, oils, other impurities such as silicon carbides, and the native oxide at the surface of waste silicon particles[13].

Silicon byproducts from sources such as kerf are difficult to use directly in lithium-ion batteries since key parameters such as silicon particle size, surface oxides, and impurities do not fulfill the requirements for silicon anode materials. As described in US Patent 8,034,313 and US Patent 8,231,006, it is possible to recover silicon from byproducts, such as kerf or silicon slurry, generated from the semiconductor manufacturing process. In this process, silicon particles are separated from kerf or slurry by sedimentation centrifugation, filtration centrifugation, and

hydro-cyclone separation. The waste silicon may be processed to recover the raw material used in solar crystals. US Patent 6,780,665 describes methods of centrifuging, decanting, filtration, froth flotation and high energy electrical discharge techniques to recover crystalline silicon metal kerf from wire saw slurries for use in thin-layer photovoltaic cell configurations.

The aforementioned processes only focus on purifying and recovering crystalline silicon from kerf or silicon slurry for photovoltaic cell purposes. No methods on silicon particle size restriction or separation and purification for battery purposes have been reported. Thus, there exists great value in recovering silicon from silicon manufacturing processes for use as battery anode material. A method to recycle the byproducts, such as kerf or polishing waste, and create anodes for lithium ion batteries is presented.

2 EXPERIMENTAL

One hundred grams of silicon slurry (approximately 50 vol.% diameter larger than 2 micrometers and approximately 50 vol.% diameter ranging from 0.5 micrometer to 100 nanometers) were mixed with 100 milliliters of anhydrous methanol as a co-solvent in a 2-liter ceramic ball mill container with 75 grams of stainless steel balls (average diameter 4 millimeters). The resulting mixture was milled for 8 hours at 25 degrees Celsius.

The resulting slurry was heated under an inert atmosphere to evaporate the co-solvent. Light silicon particles were carried away from the slurry in the form of an aerosol, leaving heavy silicon carbide, silicon, polyglycol solvent and other impurities in the slurry. The silicon particles were captured by condensation of the aerosol vapor in a buffer container. The silicon particles obtained from the abovementioned process had a diameter less than 500 nanometers. Approximately 10 grams of silicon particles can be obtained from the process described above.

Approximately 0.5 grams of the recovered silicon particles were cleaned via 10 milliliters of 1% hydrofluoric acid aqueous solution, followed by rinsing with 10 milliliters of de-ionized water three times. The silicon particles were heated at 75 degrees Celsius under argon atmosphere until completely dry.

The cleaned particles were surface modified as described in previous work [14]. The surface modified silicon nanoparticles (EMSiL) were then well mixed with 0.5 grams of carbon black (average particle size below 50 nanometer), 3.5 grams of natural graphite (average particle size below 40 micrometer), and 10 milliliters 5 wt. % polyvinylidene fluoride in n-methylpyrrolidone solution (equivalent to 0.5 grams of polyvinylidene fluoride). The

resulting mixture was applied to a copper foil (~25 micrometer in thickness) via doctor blade method to deposit a layer of approximately 100 micrometers. The film was then dried in a vacuum at 120 degrees Celsius for 24 hours.

The resulting anode was assembled and evaluated in a CR2032 lithium secondary coin cell. A disk of 1.86 cm² was punched from the film as the anode. The anode active material weight was approximately 5 micrograms. The counter electrode was a lithium metal disk with a thickness of 100 micrometers and had the same surface area as the anode. A microporous trilayer polymer membrane was used as a separator between the two electrodes. Approximately 1 milliliter of 1 molar LiPLi₆ in a solvent mix comprising ethylene carbonate and dimethyl carbonate with a 1:1 volume ratio was used as the electrolyte in the lithium cell. All of the above experiments were carried out in a glove box system under an argon atmosphere with less than 1 part per million water and oxygen.

The assembled lithium coin cell was removed from the glove box and stored in ambient conditions for another 24 hours prior to testing. The coin cell was charged and discharged at a constant current of 0.5 mA at a rate of approximately C/5 from 0.05-1.5 V versus lithium at 70% DoD for over 50 cycles.

3 RESULT AND DISCUSSION

Silicon nanoparticles can be successfully obtained through this process. As shown in Figure 1, silicon particles in silicon waste are not uniform and have a diameter in the micrometer range before treatment. After the series of steps as presented in this work, silicon nanoparticles are resized to below 300 nanometers and surface modified for use as a high capacity lithium ion battery anode material.

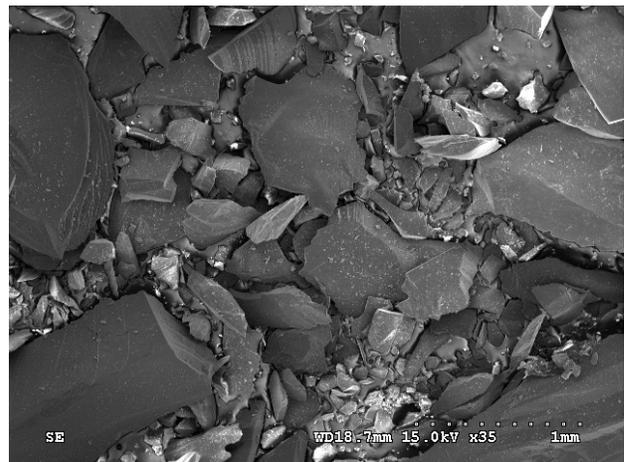


Figure 1. SEM image of saw dust generated from silicon processing, particle size is approximately 1mm

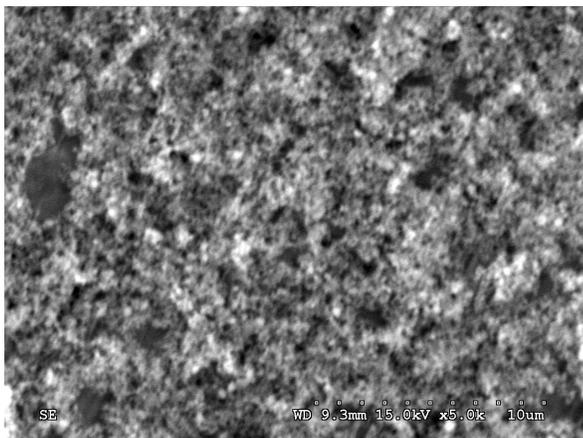


Figure 2. SEM image of resized and separated silicon particles (24hrs) from saw dust, particle size below 300 nanometers

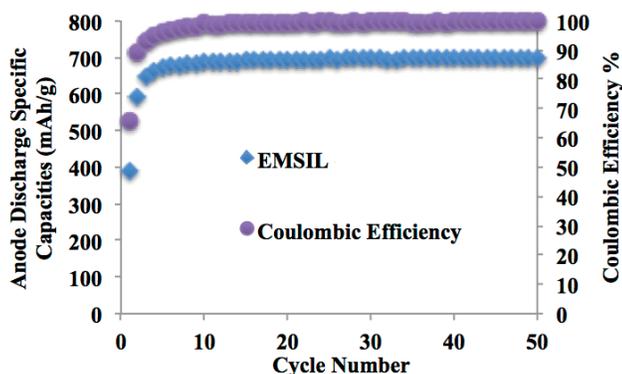


Figure 3. Anode specific discharge capacity and coulombic efficiency versus cycle number for EMSiL composite anode

Charge and discharge tests demonstrated cycle performance for composite anodes comprised of EMSiL. At 70% DoD, the initial coulombic efficiency is approximately 60% and initial discharge capacity of composite anode with less than 12% EMSiL is less than 400 mAh/g. This high initial capacity loss is attributed to the solid electrolyte interphase formation of the silicon anode. As the cell cycles, anode discharge capacity and coulombic efficiency gradually improves. After 10 cycles, discharge capacity is stabilized to around 650 mAh/g and coulombic efficiency is approaching 100%.

In summary, a method to fabricate high performance silicon anodes for lithium ion batteries is presented in this work. Through this procedure, silicon waste from semiconductor manufacturing can be recovered and treated to produce surface modified silicon nanoparticles for use as anode material for lithium ion rechargeable batteries. Specific anode capacity can be maintained at 650 mAh/g for over 50 cycles at 70% DoD.

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