# Baseline Si electrode fabrication and performance for the battery for Advanced Transportation Technologies Program
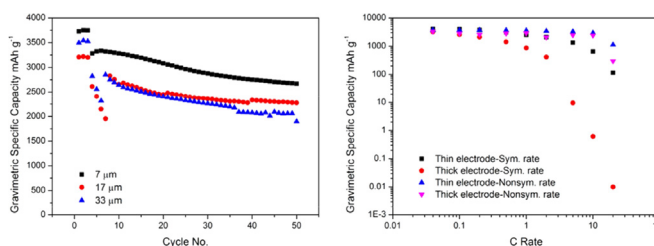
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## HIGHLIGHTS

- Baseline Si electrodes were developed and characterized.
- Study of electrode thickness influencing batteries electrochemical performance.
- Low temperature study of Si-based lithium ion batteries.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## ABSTRACT

Baseline Si electrodes were developed and characterized based on Si nanomaterials. Silicon (Si) with a designed nanostructure has attracted much attention as potential anode materials for lithium-ion batteries due to its high gravimetric specific capacity. Because of a resulted poor tap density of Si from the electrode while using nano-sized Si and also from including other additives like conductive carbon and binder, it is difficult to maintain a high loading of active materials at the anode side in lithium-ion batteries. In this report, we aim to investigate how the thickness of Si-based electrode influences the cycling performance, rate performance and impedance. We also discuss the variation of gravimetric, area and volumetric capacity along with increasing of electrode thickness. It is found that with a thinner electrode of 7 μm the volumetric capacity could reach up to 920 mAh cm$^{-3}$ but a poor area capacity of 0.7 mAh cm$^{-2}$, while a thicker one of 33 μm enables to provide a high area capacity up to 1.5 mAh cm$^{-2}$ and gives a volumetric capacity less than 500 mAh cm$^{-3}$. A cell operated under 0 °C shows a gravimetric capacity of 2000 mAh g$^{-1}$ after 60 cycles.

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## 1. Introduction

Silicon (Si) has been extensively studied as one of the most promising anodes for Li-ion batteries because of its delivering a greater theoretical gravimetric specific capacity (4200 mAh g$^{-1}$) over the conventional graphite anode (372 mAh g$^{-1}$) [1—3]. For a volumetric comparison, graphite has a theoretical volumetric capacity about 850 mAh cm$^{-3}$. For a typical 20 vol % Si electrodes discussed in Beattie's previous report, it has a volumetric energy density of 1668 mAh cm$^{-3}$ [4]. The gravimetric energy density of Si electrode at the laminate level can easily exceed 3000 mAh g$^{-1}$ (excluding the current collector), based on classic electrode design, which includes 90% (by weight) graphite, 10% of polymer binder and acetylene black (AB) conductive additive, and 30% porosity. This would be ten times higher than that of the graphite based electrode with the same composition and design. Practical volumetric energy density of graphite electrode is around 400 mAh cm$^{-3}$ using classic electrode design [5]. Switching from

graphite to Si could potentially improve the volumetric energy density in lithium-ion batteries beyond 1000 mAh cm$^{-3}$ [5–8].

As forming a Li$_{4.4}$Si alloy from lithium intercalating into Si, a 320% huge volume expansion occurs when full lithiation on Si [2,9,10]. This large volume change leads to a destructive pulverization of Si as well as electrical contact loss between active materials, which eventually cause a fast capacity fading of battery [2,11,12]. Si nanostructure designing by taking the advantages of large surface area and porosity, greatly alleviates the mechanical stress during volume changing as well as enhances the electronic connections. The successful examples include Si nano particles, [13–15] Si nanowires, [6,16] Si/C nanocomposites, [17,18] and nanoporous Si [19–22] which effectively addressed the challenge of volume change during lithiation and gave a stable cycling performance of batteries. Unfortunately, such a nano Si structure along with a high porosity packed inefficiently with a low stacking density, which would lower the volumetric energy density, and need to increase the loading of other components including binder and conductive agent leading to more side reactions. High energy density battery with an ordered-structure like Si nanowires has been demonstrated to exhibit a high volumetric energy density in lithium-ion batteries, especially combing with carbon to form Si/C composite electrode. Very few examples have been reported on achieving both a high area and volumetric capacity so far. Cui and coworker first developed freestanding nanocomposites made of carbon nanofibers (CNFs) and silicon nanowires (SiNWs) as metal current collector-free anode platforms. This achieved an improved areal capacity up to 5 mA cm$^{-2}$ and a corresponding volumetric capacity of 1429 mAh cm$^{-3}$ [5]. Later on, Cho reported a new architecture consisting of SiNWs internally grown from porous graphite, providing more free spaces to accommodate volume expansion of internally grown Si during cycling and facilitate electron transport as well. With this strategy, the electrode has a high density of 1.5 g cm$^{-3}$ and the prepared battery exhibits a high volumetric capacity of 1363 mAh cm$^{-3}$ with high initial coulombic efficiency over 90% [6]. Very recently, Cui's group designed a pomegranate-inspired nano structure with void space around single Si nanoparticles in an encapsulated thicker carbon layer, which enable to leave a buffering room for Si expansion and contraction. After continued lithiation/delithiation, the solid-electrolyte interphase (SEI) layer remained stable with high capacity retention over 97% after 1000 cycles. And the cycling performance remained stable even when the area capacity increased above 3 mAh cm$^{-2}$ [7].

Considering complex manufacturing process and high cost of nano-sized Si, and Si large volume expansion, it is very challenging to develop a Si based material and electrode assembly approach for a practical high capacity Si electrode. In this study, we selected commercial available pure nano-sized silicon particles, sodium carboxy methyl cellulose (NaCMC) binder and acetylene black to make baseline composite electrodes. Charge/discharge cycling performance, rate performance has been studied while applying different thickness of anodes, especially a full discussion on variation of corresponding gravimetric, area and volumetric specific capacity. This effort is part of the US DOE's Battery for Advance Transportation Technologies program R&D effort to develop advanced high capacity Si anodes. Baseline Si based electrodes developed at Lawrence Berkeley National Laboratory provide a benchmark for the comparison study of variety of the materials and electrodes developed under the BATT[2] program.

## 2. Experimental

The nano-sized Si particles were experimental sample name Si Nano-Grain from Umicore. Acetylene black as conducting agent was purchased from TIMCAL. To make a baseline electrode, a slurry including n-Si particles (50 wt %), carboxyl methyl cellulose binder (20 wt %), poly vinyl alcohol (PVA) (5 wt %) and acetylene black (25 wt %) in aqueous solution was homogenized for one hour. The uniform slurry was cast on copper foil. The thickness of electrodes was controlled by doctor blade gap to achieve the desired area capacity loading. Electrolytes were purchased from Novolyte (now part of BASF), including battery-grade lithium hexa-fluorophosphate (LiPF6) in ethylene carbonate (EC), diethyl carbonate (DEC) and fluoroethylene carbonate (FEC). The composition of electrolyte is 1 M LiPF$_6$ in EC:DEC = 1:1 with 10% FEC by weight. For A Celgard 3501 Separator membrane was purchased from Celgard. Other chemicals were purchased from Sigma Aldrich and used without any further purification. Coin cells were prepared with lithium metal (purchased from FMC Corporation) as counter electrode. The cell fabrication can be found in the literature [23]. The coin cell performance was evaluated with a Maccor Series 4000 Battery Test System in a thermal chamber at 30 °C. For the low temperature study, battery cycling test was performed at 30 °C for 1° cycles and switched to 0 °C for the rest of 50 cycles at C/10. The C-rate calculation of the Si based electrode is assuming the Si has the theoretical capacity of 4200 mAh g$^{-1}$. Electrochemical Impedance Spectroscopy (EIS) were conducted on a VMP galvanostat/potentiostat (Bio-Logic). Si half cells were cycled for 50 complete cycles at a C/10 rate, followed by a half lithiation at one extended cycle and rested for 4 h before EIS measurement. The sample cells were brought to 10 mV before impedance measurement was taken at 0.01 Hz to 0.1 MHz.

## 3. Results and discussions

A commercial available n-Si nanoparticle has been selected as an active material. A corresponding laminate (or composite electrode) was made of 50wt% Si, 25wt% Acetylene black and 25 wt% polymer binder (20 wt% sodium carboxy methyl cellulose (NaCMC) plus 5 wt % Poly vinyl alcohol (PVA)). The pristine Si particles have sphere structure everywhere with a large size distribution from 50 nm to 200 nm. Prepared composite electrode has exhibited large porosity which provides lots of voids for large volume expansion during charge/discharge of Si. The Si particles are glued by a commercial NaCMC binder and electrical connected by AB particles.

The electrochemical performance with different thickness of Si electrode was shown in Fig. 1. Three laminates have been prepared with the thickness of 7 μm, 17 μm, and 33 μm respectively. The electrodes were made with doctor blade coating. And the labeled electrode thicknesses in the figures and text are from dry electrode laminates, not the doctor blade gap. Corresponding Si loading and electrode porosity are calculated and listed in Table 1. While increasing the thickness, the packing efficiency of Si particles in the electrode becomes less efficient with a larger porosity. Especially an electrode with 33 μm thickness holds a porosity of 78%, which would potentially accommodate more Si volume expansion during lithiation. For a better comparison, all cells under testing were made of cells using Li metal as the counter electrode. As seen in Fig. 1a, all three cells showed a very similar capacity fading trend. In the very beginning, a slow lithiation rate of C/25 is applied at least for three cycles for SEI formation followed by a relatively fast rate of lithiation of C/3 and delithiation of C/2 for the rest of the cycling. It is observed that faster fading occur at the first 20 cycles and become more stabilized at extended 30 cycles. It is interesting to see the thinnest electrode of 7μm always gives the best performance of