Si alloy/graphite coating design as anode for Li-ion batteries with high volumetric energy density

Zhijia Du*, Jianlin Li, C. Daniel, D.L. Wood III

Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ABSTRACT

A simplified mathematical model is developed for designing high-energy-density Si alloy/graphite coatings. The design is discussed based on a set of metrics related to their implementation in practical cells including volumetric capacity, average voltage, volumetric energy density, particle expansion, and cell expansion. To achieve the same energy density improvement, one can use either high capacity Si alloys at a lower weight ratio in Si alloy/graphite coatings or low capacity Si alloys at a higher weight ratio. However, high capacity Si alloys have high volume expansion at the particle level, which tends to have SEI stabilization issues, while low capacity Si alloys lead to high volume expansion at cell level. Gravimetric energy density is also calculated in the model, and it is found that the energy density improvement based on a gravimetric basis is smaller than that of a volumetric one. The findings from this model are highly beneficial for Si alloy/graphite coating design for achieving maximum energy density with respect to the volume expansion issue.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The development of Li-ion cells with high volumetric energy density is of great technological importance for consumer electronics [1] and automotive applications [2]. Much attention has been given to Si-based materials due to the high theoretical capacity of Si (2194 Ah/L, compared to 764 Ah/L of graphite) [3]. However, this high capacity is associated with large volume expansion during lithiation of Si. The volume expansion ruptures the solid electrolyte interphase (SEI) layer during progressive cycling and exposes fresh surfaces of Si to the electrolyte [3,4]. This leads to the reduced coulombic efficiency (CE) due to consumption of active Li$^+$ inventory in a full cell. Calculation has shown how capacity fade in a full cell can quickly become unacceptable because of only small changes in the CE [3]. One way to circumvent this problem is the use of active/inactive alloys. The design principles of active/inactive alloys have been reported by Obrovac et al. who found the molar volume of lithium is about 9 mL/mol [1]. One example of this type of material is the Si alloy class developed by 3 M Company, which are micron-sized particles constituted of nano-sized Si domains well dispersed in an inactive phase. This material class has been found to outperform the stand-alone nano-sized Si particles [5].

In addition to the active material R&D on Si alloys, other important progress has also contributed towards the application of Si alloys in Li-ion cells such as the electrode binder and electrolyte. It has been shown that good binders should have strong bonding to Si particles and uniformly cover their surface [3,6,7]. Electrodes using binders with carboxylic acid sites have shown good cycling performance, such as carboxymethyl cellulose (CMC) [6], lithiated polyacrylate (LiPAA) [7,8], and alginate [9]. Rationally designed conductive polymers have also been shown by Liu et al. to be excellent binders for Si-based electrodes [10,11]. The cycling performance of Si alloys is highly dependent on electrolyte composition as well. It is generally recognized that the addition of fluoroethylene carbonate (FEC) to conventional electrolytes can remarkably improve cycling performance [12–14], which is due to formation of a more stable and thinner SEI and suppression of electrolyte decomposition. From these two major contributions, Si alloys have been shown to cycle several hundred times in Li-ion cells [15].

With notable cycle life now achieved for Si alloy materials, two questions need to be answered: 1) what is the best way to incorporate Si alloys in anode coatings; and 2) how much energy density improvement in a lithium-ion full cell can be achieved? Thus, a rational design strategy must be developed regarding the

List of Nomenclature

F	Faraday constant, 96485 C/mol
k	Molar volume of lithium in Si alloys, 9 mL/mol [1]
M_M	Molar mass of inactive M ($FeSi_2$), 112.015 g/mol
M_{Si}	Molar mass of Si, 28.085 g/mol
n/p	N/P ratio, 1.1
q_C	Capacity of graphite (based on LiC_6), 372 mAh/g
q_{NMC}	Specific capacity of NMC532, 160 mAh/g
q_{Sia}	Specific capacity of Si alloy, mAh/g
q_{SiaC}	Specific capacity of graphite and Si alloy mixture, mAh/g
q^+	Areal capacity of the cathode, mAh/cm^2
q_{NMC}	Volumetric capacity of NMC532, 768 mAh/mL
q_{Sia}	Volumetric capacity of Si alloy, mAh/mL
q_{SiaC}	Volumetric capacity of graphite and Si alloy, mAh/mL
t^+	Cathode thickness, 55 μm
t^-	Anode thickness at full lithiation, μm
t_0^-	Anode thickness at full de-lithiation, μm
t_{Al}	Thickness of the current collector (Al foil), 15 μm
t_{Cu}	Thickness of the current collector (Cu foil), 15 μm
t_s	Thickness of the separator, 20 μm
$\bar{U}$	Volumetric energy density of the cell stack, Wh/L
V_C	Delithiation voltage of graphite, 0.125 V (vs. Li$^+$/Li)
V_{Si}	Delithiation voltage of Si, 0.415 V (vs. Li$^+$/Li)
V_{Sia}	Delithiation voltage of Si alloy, 0.415 V (vs. Li$^+$/Li)
V_{SiaC}	Delithiation voltage of graphite and Si alloy in anode, V (vs. Li$^+$/Li)
V_{NMC}	Lithiation voltage of NMC532, 3.8 V (vs. Li$^+$/Li)
w^+	Area mass of cathode, g/cm^2
w^-	Area mass of anode, g/cm^2
w_{Al}	Area mass of the current collector (Al foil), 4.05 mg/cm^2
w_{Cu}	Area mass of the current collector (Cu foil), 13.44 mg/cm^2
w_e	Area mass of the electrolyte, 6.15 mg/cm^2
w_s	Area mass of the separator, 1.08 mg/cm^2
x	Mole ratio of active Si in Si alloy
ξ_C	Volume expansion ratio of graphite at full lithiation, 10% [33]
ξ_{Sia}	Volume expansion ratio of Si alloy at full lithiation
ξ_{SiaC}	Volume expansion ratio of graphite and Si alloy at full lithiation
ξ_{cell}	Volume expansion ratio of the cell stack
ρ_C	Density of graphite, 2.266 g/mL
ρ_M	Density of inactive M ($FeSi_2$), 4.96 g/mL
ρ_{NMC}	Density of NMC532, 4.8 g/mL
ρ_{Si}	Density of Si, 2.3 g/mL
ρ_{Sia}	Density of Si alloy, g/mL
ρ_{SiaC}	Average density of graphite and Si alloy, g/mL
ϕ^+	Cathode porosity, 0.3
ϕ^-	Anode porosity, 0.3
ω_{Si}	Weight ratio of active Si in Si alloy
ω_{Sia}	Weight ratio of Si alloy in graphite and Si alloy mixture in anode

volumetric energy density of these cells. Commercial electrodes are typically densified via calendering under high pressure [16,17]. A recent study by Du et al. investigated the effect of calendering electrodes containing Si alloy particles [18]. They showed non-calendered Si-alloy coatings had no gain in volumetric energy density compared to graphite coatings while calendered anodes showed poor cycling performance due to binder damage.

Therefore, graphite was added to Si-alloy anodes to provide lubrication during calendering. The use of calendered Si-alloy/graphite anodes in the place of graphite resulted in an increase of 15% in energy density in full cells with $LiCoO_2$ cathodes [18].

It is well-known that high capacity Si alloys expand considerably during lithiation. The calculation of volumetric energy density should be based on the electrode volume at full lithiation [1,3,18], but the electrode volume without the impact of lithiation (expansion) has often been used to calculate volumetric capacity [19–21]. A recent publication inaccurately stated that the volume expansion of Si can be accommodated by existing pores in the electrode and there is no increase in thickness upon lithiation [22]. However, Du et al., found that the porosity of the electrode was almost the same before and after lithiation, indicating that Si alloys do not expand into the pores [18]. This has been confirmed in several recent reports where the pores were found to expand by a similar ratio to the particles in the electrode [23–25].

Since Si-based materials are on the R&D roadmaps of most of major lithium-ion cell manufacturers, the objective of this study is to develop a Si alloy/graphite anode design model with the motivation of improving the volumetric energy density of full cells. Such information is scarce and is not included in the most recent version of the Argonne National Laboratory BatPac model [26]. The effect of volume change on cell performance is discussed at both the active material and cell levels, and an opportunity is provided for the development of practical Si alloy/graphite coatings with high energy density, moderate particle expansion, and moderate cell expansion.

2. Method and Model

2.1. Si alloy particle principles

Si alloys have been extensively reported with respect to the "active/inactive" concept where the volume expansion of Si could be diluted by inactive components [1]. The inactive component is also beneficial to the electrochemistry of Si, which could suppress the formation of $Li_{15}Si_4$ [27–29]. The cycling performance is improved because there is no particle fracture induced by a two-phase reaction front. A typical formula is written as $Si_x[M]_{1-x}$, where x is the "atomic ratio of active Si" and M is "inactive phase in the alloy". $FeSi_2$ is used as an example for the particle level calculation. The density of the Si alloy (ρ_{Sia}) is given by (see List of Nomenclature for definitions of terms):

$$\frac{1}{\rho_{Sia}} = \frac{\omega_{Si}}{\rho_{Si}} + \frac{1 - \omega_{Si}}{\rho_M} \tag{1}$$

The weight ratio of Si in the Si alloy (ω_{Si}) is given by:

$$\omega_{Si} = \frac{xM_{Si}}{xM_{Si} + (1 - x)M_M} \tag{2}$$

The specific capacity of the Si alloy (q_{Si}) is given by taking 3.75 Li atoms per Si atom:

$$q_{Sia} = \frac{3.75[mol] \times F \times [mAh/3.6C] \times \omega_{Si}}{M_{Si}} \tag{3}$$

A problematic characteristic of Si alloy particles during lithiation is the volume expansion, which leads to particle and SEI layer fracture and consumption of more active Li in the cell at the freshly exposed surface due to formation of new SEI. Cycling performance has been shown to be related to the volume expansion ratio of Si alloy particles. Particles with reduced volume expansion have better cycling performance, and vice versa [28,30]. It is important to have the volume expansion ratio of the Si alloy particles and the volumetric capacity. Obrovac et al. have shown