

Alloy Design for Long Term Cyclability of Si Based Anode Materials for Lithium Ion Batteries

Moni Kanchan Datta and Prashant N. Kumta

University of Pittsburgh

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ABSTRACT

Composites comprising silicon (Si), graphite (C) and polyacrylonitrile based disordered carbon (PC), denoted as Si/C/PC, have been synthesized by thermal treatment of high energy mechanically milled silicon, graphite, and polyacrylonitrile (PAN) powder of nominal composition 42wt.%C-28wt.%Si-30wt.%PAN. The resultant Si/C/PC composite exhibits a 1st charge capacity of ~1015mAh/g with a fade in capacity ~0.31% per cycle when cycled at a rate of ~160mA/g. In order to improve the cyclability of the Si/C/PC composite system, the alloying/dealloying behavior of lithium ion with silicon has been studied to minimize the volume expansion/contraction during electrochemical cycling, and accordingly changes in the alloy composition has been proposed to fulfill the requirements for practical application.

INTRODUCTION

Rechargeable lithium ion batteries with silicon as an anode has gained tremendous interest due to its high theoretical specific capacity (~4200mAh/g), rendering it a possible candidate electrode for next generation Li-ion batteries to be used in the modern portable electronic devices as well as for hybrid electrical vehicles. However, the high specific capacity Si based anode materials undergoes a large volume expansion/contraction cycle (~117-311%) during electrochemical cycling due to the repeated alloying and dealloying processes of Si with lithium ion to form different kinds of intermetallics or amorphous phases [1,2]. This large volume expansion/contraction leads to the mechanical failure of the Si based electrode during alloying and dealloying processes of Li with Si, and as a result the Si based anode materials show poor capacity retention due to loss of electrical contact between the cracked and isolated separated Si particles and the current collector [2,3]. In order to improve the stability of the electrode (i.e. capacity retention) of Si based anode materials, the active/inactive composite concept has been utilized to improve the mechanical properties of the materials where electrochemically active Si is

homogeneously dispersed and distributed within a suitable matrix [4-7]. Different categories of Si based composites have recently been generated. These systems synthesized with different kind of matrix by different synthesis technique show improved cyclability with respect to pure silicon [4-13] mainly due to the enhancement in the mechanical properties. In addition, use of nanocrystalline silicon instead of microcrystalline Si is also expected to improve the capacity retention in some degree [12,13]. However, the retention in capacity, reported in various articles [4-13], of Si based anode materials using composite structure even with nanocrystalline silicon as dispersoid is still not suitable for use in commercial application due to the high degree of capacity fade per cycle (> 0.1% loss per cycle).

Therefore, in addition to improving the mechanical properties of silicon based composite materials, the system poses a formidable challenge to materials scientist to reduce the volume expansion/contraction during repeated alloying and dealloying processes of Si with Li in order to obtain long term stability of Si based anode. Fig. 1 shows the expected theoretical volume expansion/contraction of Si along with expected theoretical specific capacity to form different equilibrium Li-Si based intermetallics in a single reaction step. The formation of lowest Li content intermetallics ($\text{Li}_{12}\text{Si}_7$) is even expected to undergo ~117% volume expansion (Fig.1) which will be sufficient to form cracks or result in mechanical failure of the electrode materials. In order to minimize the volume expansion/contraction during alloying and dealloying processes, one has to synthesize highly expanded Si crystal or amorphous Si of molar volume (~100-300% higher than crystalline silicon) closer to the molar volume of Li-Si based intermetallics. Fig. 1 also shows the expected volume expansion during alloying of Li with Si in each and every single step of the alloying/dealloying occurs according to the equilibrium phase diagram. Fig. 1 clearly suggests that the volume expansion/contraction during alloying and dealloying processes could be minimized if the electrochemical cycling is restricted between the Li-Si based intermetallics rather than pure silicon as anode material. For example, continuous reversible alloying and

de-alloying of Li with the Li-Si intermetallics, Li_7Si_3 to form $\text{Li}_{22}\text{Si}_5$ is expected to undergo a volume expansion of only ~60% with a specific capacity ~1270mAh/g, although the potential window would need to be examined for possible practical applications.

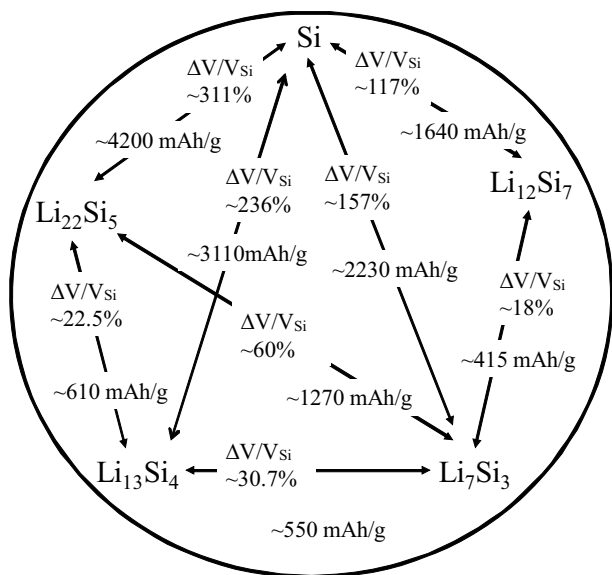


Fig.1: Theoretical volume expansion/contraction of Si along with expected theoretical specific capacity to form different equilibrium Li-Si based intermetallics.

Therefore, in order to design Si based alloy compositions as an anode that can yield high specific capacity with excellent cyclability for lithium ion battery application, it is of paramount importance to minimize the volume expansion/contraction during alloying and dealloying processes combined with improved mechanical properties. In this regard, it is important to understand the alloying/dealloying behavior of lithium with silicon during electrochemical cycling, which will accordingly provide guidelines to design the perfect alloy composition to fulfill the requirements for practical application. In the present study, silicon and graphite based composite has been used to study the cycling behavior, and understand the influence of the starting alloy composition on the stability of Si based materials. Si/C based composite has been used instead of pure microcrystalline Si because pure Si as mentioned earlier undergoes failure within few cycles which is not suitable for studying the long cycle life. In this regard, graphite and Si based phase mixture or Si/C composite could be a good model structure for studying the electrochemical behavior due to its higher specific capacity than pure graphite and better cyclability than pure silicon. In recent years, Si/C based composite has been explored by our research group largely generated using high energy mechanical milling of Si and graphite in the presence of different types of polymers [6-8,10]. The polymer acts as a diffusion barrier during high energy milling between Si and graphite preventing the formation of the electrochemically inactive SiC during mechanical milling as well as after thermal treatment up to ~1073-1173K. The Si/C composite coated with polymer based

amorphous hard carbon obtained after thermal treatment of mechanically milled powder shows high reversible capacity (~600-700mAh/g with a current rate of 160mA/g) with excellent cyclability [6-8,10]. In the present article, recent research results on Si and graphite based composite materials of nominal composition 42wt.%C-28wt.%Si-30wt.%PAN has been presented which mainly address the alloying/dealloying behavior of Si with Li during electrochemical cycling of the electrode at different potential windows to identify the most stable phase field which exhibit excellent electrochemical performance. Results of these studies with appropriate alloy design propositions are discussed in the following sections.

EXPERIMENTAL DETAILS

MATERIALS SYNTHESIS

Mixtures of elemental powders of synthetic graphite (Aldrich, 1-2 micron), Si (Alfa aesar, -325 mesh) and polyacrylonitrile (PAN) of elemental composition 42wt.% C-28wt.% Si-30wt.% PAN were subjected to mechanical milling in a high energy shaker mill (SPEX CertiPrep 8000M) up to 12h in a stainless steel (SS) vial using 20 SS balls of 2mm diameter (~ 20g) with a ball to powder weight ratio 10:1. Specifically, ~0.6g of PAN was dissolved in ~10ml *N*-methylpyrrolidinone (NMP) to form a homogeneous solution. Graphite (~0.84g), Si (~0.56g), and the PAN solution were batched in a vial inside an argon filled glove box (Vacuum Atmosphere HE-493, ~10 ppm oxygen and ~0.10 ppm moisture) in order to prevent oxidation of the reactive components during milling. The PAN solution keeps the ingredients and grinding balls completely submerged in the vial. This was helpful to avoid excessive cold welding; agglomeration and temperature build up during milling [14] which is deleterious to the electrochemical response. In order to decompose the PAN to form PAN based carbon (PC) [6], the mechanically milled powders were annealed isothermally at 1073K for 6h in an ultrahigh purity argon (UHP-Ar) atmosphere using a heating rate 10K/min and a flow rate of 100 mL/min.

MATERIALS CHARACTERIZATION

In order to perform qualitative phase analysis, the milled powders as well as heat treated powders were characterized by x-ray diffraction (XRD) using the Philips XPERT PRO system employing the CuK_α ($\lambda=0.15406\text{nm}$) radiation. Electrochemical characteristics were analyzed from electrodes that were prepared by mixing 82 wt % of the active powder of -325 mesh and 8 wt % acetylene black. A solution containing 10 wt % polyvinylidene fluoride (PVDF) in *N*-methylpyrrolidinone (NMP) was added to the mixture. The as-prepared solution was coated onto a Cu foil. A 2016 coin cell design was used employing lithium foil as an anode and 1 M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC=1:2 in volume) as the electrolyte. All the cells tested in this study were cycled at room temperature