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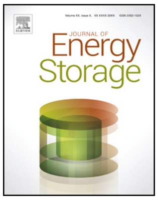

Theoretical optimization of electrode design parameters of Si based anodes for lithium-ion batteries

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ABSTRACT

Silicon is considered one of the most promising anode materials for next-generation lithium-ion batteries. However, dramatic volume expansion during the lithiation of silicon complicates its practical implementation. Literature reports nanostructured electrodes, which are capable to accommodate the volume expansion, reducing associated swelling, degradation and capacity fading. However, several phenomena associated with the volume expansion, such as the reduction of the electrode's porosity, are inherent to the system and must be carefully considered for targeted engineering of high-energy lithium-ion batteries. Herein, we determine design criteria of silicon based electrodes, taking into account the volume expansion during lithiation. A "deformation threshold" is defined signifying the minimum value of the initial porosity that must be adjusted to avoid plastic deformation and dramatic reduction of the electrode's porosity during charging. In addition, a "C-rate threshold" is defined, guaranteeing diffusion limited currents not falling below a desired discharge rate. The impact of these theoretical limitations on the electrochemical performance of silicon-based electrodes is analyzed from an engineering point of view. The derived relations are used to optimize the electrode design parameters regarding maximum gravimetric and volumetric capacity.

1. Introduction

In the recent years, silicon (Si) has attracted intense attention as suitable anode material for next generation lithium-ion batteries (LIBs). Si offers both a low electrode potential vs. Li/Li^+ (0–1 V) and a high theoretical gravimetric capacity (4200 mAh g_{Si}^{-1}) in comparison to common graphite-based anodes (372 mAh g_C^{-1}) [1–3]. However, several challenging issues emerged during the development of Si based anodes. Si based electrodes can exhibit significantly higher irreversible capacity and lower coulombic efficiency compared to conventional graphite anodes, which may lower the practical capacity and cycle life performance [4,5]. Moreover, the volume expansion of 300 – 400% during the lithiation of Si causes several challenging issues regarding mechanical stress and degradation, and swelling of the battery pack during operation, which complicates the practical implementation of Si as an anode material in LIBs [4,6–8]. Fundamental studies that have been conducted to understand structural and volumetric changes, stress evolution, mechanical properties, and fracture behavior of nanostructured Si anodes have recently been reviewed [9]. Repeated volume changes during cycling cause loss of electrical contact between individual active material units and the current collector [10]. Furthermore, the volume expansion of Si causes disruption and subsequent recreation of the solid electrolyte interphase layer [4,7], as well as fracture and pulverization of Si/alloy particles [11], resulting in capacity fade.

However, due to the very promising properties of Si, tremendous efforts have been made to tackle these critical issues. The acquired approaches include e.g. the nanostructuring of Si [1,12–14], targeted porosity tailoring [15,16], and graphite blending [17–19] to accommodate the volume expansion. The resulting electrodes reveal outstanding electrochemical performance regarding the specific capacity, e.g. in mAh g_{Si}^{-1}, related to the mass of active material used.

However, from the engineering point of view, we are interested in the energy density, e.g. scalable in Wh kg^{-1}, related to the total mass of the electrode or cell. The mass of the electrode includes the active material(s), the loading of the pores by liquid electrolyte, binder and conductive additives and some kind of current collector. Thus, the energy density of the electrode depends on

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the mass ratio of active to inactive materials used. Common technological approaches to increase the energy density of porous insertion electrodes include the increase of the electrode thickness (active material/current collector ratio) and the decrease of the porosity (electrolyte/active material ratio). However, both increasing the electrode thickness and decreasing the porosity reduce the power density due to increased limitations of lithium transport inside the electrode [20,21]. Additionally, the degree of graphite blending affects both the attainable capacity and the mean volume expansion of the composite electrode [24]. Therefore, optimizing these design parameters is a critical issue for the development of high-energy and high-power LIBs [4].

In this theoretical study, we determine optimum design criteria of porous Si based electrodes, taking into account the volume expansion during lithiation, the degree of graphite blending and different limits of swelling. For this purpose, a "deformation threshold" is defined, signifying the minimum value of the initial porosity that must be adjusted to avoid plastic deformation and dramatic reduction of the electrode's porosity during charging. Furthermore, a "C-rate threshold" is defined, guaranteeing diffusion limited currents not falling below a desired C-rate and thus avoiding massive reduction of the capacity during rapid charging. The impact of these design restrictions on the performance parameters of Si based anodes is analyzed. Moreover, the derived relations are used to optimize the electrode design parameters regarding gravimetric and volumetric capacity.

Hereinafter we consider porous Si based electrodes of arbitrary design blended with varying amounts of graphite. This includes different nanostructures, e.g. nanorods, nanotubes, nanoparticles, etc. on a two-dimensional current collector foil or some sort of three-dimensional current collector, e.g. copper foam. Non-porous electrodes, as e.g. Si thin films, are not considered.

2. Porosity

The volume expansion associated with the lithiation of Si causes a swelling of the electrode and a decrease of the porosity. In this section, we investigate these effects by straightforward calculations of the state of charge (SoC) dependent porosity considering the volume expansion and different limits of swelling. The initial porosity, ε_0, of a porous insertion electrode of arbitrary design is given by:

$$\varepsilon_0 = 1 - \frac{\sum_i V_i}{V} \tag{1}$$

with V_i and V being the initial volumes of the solid components and the electrode. In our calculations, the solid components include variable mass fractions of silicon (Si) and graphite (C) as well as binder (B) and conductive additives (A). Assuming a linear volume expansion by n-times the initial volume between $SoC = 0$ and $SoC = 1$, the porosity of the electrode can be expressed as:

$$\varepsilon(SoC) = 1 - \frac{\sum_i V_i\,(1 + n_i \cdot SoC)}{V\ \ (1 + n_S \cdot SoC)} \tag{2}$$

In Eq. (2), n_S accounts for the permitted limit of swelling of the electrode (typically approximately 10 %). Mixing Eqs. (1) and (2) and introducing mass fractions gives:

$$\varepsilon(SoC) = 1 - \frac{(1-\varepsilon_0)}{(1 + n_S \cdot \mathrm{SoC})\sum_i \frac{\omega_i}{\rho_i}} \sum_i \left(\frac{\omega_i}{\rho_i} (1 + n_i \cdot \mathrm{SoC}) \right) \tag{3}$$

A detailed derivation of Eq. (3) can be found as Supplementary material.

Fig. 1 shows the change of the electrode's porosity during the lithiation of the electrode for different initial porosities, computed from Eq. (3). Relevant variables used for the calculations are listed at the top of Fig. 1. Parameters kept constant throughout the study are listed in Table 1.

As expected, the porosity clearly decreases with increasing *SoC*. This effect is most pronounced at low initial porosities. For initial porosities in the range of 20–40 %, which is typical for commercial graphite electrodes, the porosity of a Si based electrode would rapidly decrease to zero during charging. Such a process would induce enormous mechanical stress inside the electrode, causing pulverization of Si, loss of electrical contact, etc. and corresponding capacity fade. In the case of medium initial porosities of 50–70 %, the reduction of the porosity is less pronounced. However, even at these relatively large initial porosities, when compared to commercial graphite electrodes, the porosity decreases to zero before reaching $SoC = 1$. Only for very high porosities, above 80 %, the porosity at $SoC = 1$ is significantly larger than zero. This behavior is illustrated schematically in Fig. 1b.

Fig. 2a shows the porosity at $SoC = 1$ as a function of the initial porosity ($SoC = 0$) for different mass fractions of graphite and Si in the composite, respectively. Please note that $\omega_{Si} = 95\,\%$ corresponds to a pure Si electrode, whereas $\omega_{Si} = 0\,\%$ represents a pure graphite electrode (each including 3 wt% binder and 2 wt% conductive additive). The range of initial porosities resulting in total densification of the electrode during charging clearly expands with increasing amount of Si. In the case of a pure graphite

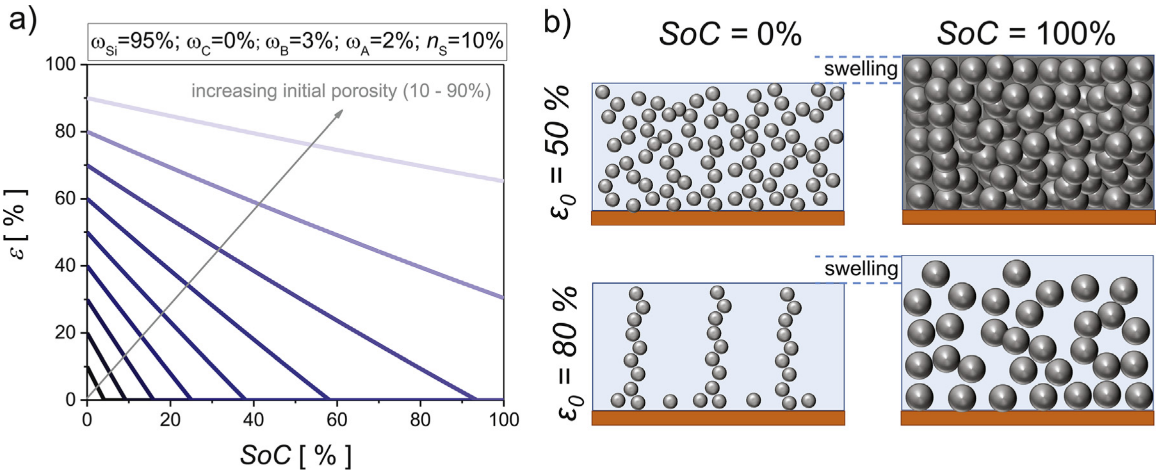

Fig. 1. a) Development of the porosity during lithiation of the electrode for different initial porosities. Relevant parameters used for the calculation are listed at the top of the figure. b) Schematic illustration of the development of the porosity for different initial porosities.