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A first-principles study on the effect of oxygen content on the structural and electronic properties of silicon suboxide as anode material for lithium ion batteries

Obaidur Rahaman [a, *], Bohayra Mortazavi [a], Timon Rabczuk [a, b, **]

[a] Institute of Structural Mechanics, Bauhaus-Universität Weimar, Marienstr. 15, D-99423 Weimar, Germany
[b] School of Civil, Environmental and Architectural Engineering, Korea University, 136-713 Seoul, Republic of Korea

HIGHLIGHTS

- We used DFT to investigate the role of Oxygen on silicon suboxide properties.
- O–Li interaction is stronger than Si–Li interaction.
- Higher O content reduces volume expansion due to lithiation.
- Lithium storage capacity is higher at high O content.

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ABSTRACT

Silicon suboxide is currently considered as a unique candidate for lithium ion batteries anode materials due to its considerable capacity. However, no adequate information exists about the role of oxygen content on its performance. To this aim, we used density functional theory to create silicon suboxide matrices of various Si:O ratios and investigated the role of oxygen content on the structural, dynamic, electronic properties and lithiation behavior of the matrices. Our study demonstrates that the O atoms interact strongly with the inserted Li atoms resulting in a disintegration of the host matrix. We found that higher concentration of oxygen atoms in the mixture reduces its relative expansion upon lithiation, which is a desirable quality for anode materials. It helps in preventing crack formation and pulverization due to large fluctuations in volume. Our study also demonstrates that a higher oxygen content increases the lithium storage capacity of the anode. However, it can also cause the formation of stable complexes like lithium silicates that might result into reversible capacity loss as indicated by the voltage –composition curves. The study provides valuable insights into the role of oxygen in moderating the interaction of lithium in silicon suboxide mixture in microscopic details.

1. Introduction

Although graphite-based anode material is commonly used in commercial production of rechargeable Lithium Ion Batteries (LIB), it has several limitations. It is relatively expensive to manufacture and a specific capacity of 372 mA h/g imposes a limitation on the energy density. Silicon-based anode materials have been the recent focus of research in this area because of its abundance, low manufacturing cost and high theoretical lithium capacity of 4200 mA h/g [1–3]. Although it is recently emerging as a replacement for carbon-based anode materials, it also has some limitations. The biggest limitation of silicon-based anode material is its large volume change (>300%) during the lithiation and delithiation process leading to crack formation, pulverization and capacity fading as a consequence of loss of electrical contact [4]. Many experiments were conducted with altered design parameters or mixing silicon with other elements with an aim to overcome this problem [5,6].

Mixing silicon with oxygen atoms is one of the proposed schemes to improve the performance of silicon-based anodes [7,8]. Kim et al. used inductively coupled plasma to investigate the effect of oxidation on the silicon oxide based anode and recommended

* Corresponding author.
** Corresponding author. School of Civil, Environmental and Architectural Engineering, Korea University, 136-713 Seoul, Republic of Korea.
E-mail addresses: ramieor@gmail.com (O. Rahaman), timon.rabczuk@uni-weimar.de (T. Rabczuk).

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the reduction of oxygen concentration below 18 atom % in order to increase the initial capacity [9]. Abel et al. designed partially oxidized (≈13 atom % O) nano-structured silicon thin films that produced a high capacity of approximately 2200 mA h/g, which was reversibly cycled for 120 rounds with practically no capacity fade and 80% of the initial reversible capacity was retained after 300 cycles [10].

Although several experimental studies were conducted in order to improve the quality of the silicon-suboxide anode material, an in-depth atomic-scale understanding of the interactions, bonding mechanism, energetic, diffusivity, mixture formations and their lithiation behavior is necessary for the rational design of silicon suboxide based anodes. Therefore, computational methods like *ab initio molecular dynamics* (AIMD) simulations are extensively used to design and investigate the performance of silicon suboxide since they can be very useful in discerning these microscopic properties [11–13].

In a recent study, Chou et al. used Density Functional Theory (DFT) to investigate the lithiation behavior of silicon-rich oxide ($SiO_{1/3}$) [11]. At high lithiation of $SiO_{1/3}$ matrices, they observed the formation of six-fold coordinated $[Li_6O]^{4+}$ clusters, as opposed to the irreversible formation of Li_2O and various lithium silicates at a higher O:Si ratio (SiO_2 for example) leading to irreversible capacity loss. They suggested that the formation of $[Li_6O]^{4+}$ clusters could be related to the Si:O atomic ratio and the O spatial distribution in the suboxide mixture. They also suggested that the capacity and cyclability could be sensitive to the structural arrangement of the suboxide mixture. Thus, fine tuning the concentration and distribution of O atoms is crucial in maximizing the performance of the silicon suboxide based anode.

Following these suggestions we conducted a systematic study of the effect of O:Si ratio on the mixture formation and structural evolution with lithiation process. Various amorphous matrices of silicon suboxide with increasing Si:O ratio were generated. The geometrical, volumetric, dynamic and energetic properties were analyzed and compared in order to illustrate their sensitivities to the Si:O ratio. The factors important for designing a silicon suboxide anode material for optimum performance in LIB are discussed.

2. Computational methods

Six amorphous silicon suboxide matrices *a*-SiO_y (y = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) were created by six independent sequences of annealing, quenching and equilibration steps. Each system contained 30 Silicon atoms and the number of oxygen atoms varied according to the Si:O ratios. For each case, two independent supercells were used to improve the statistics. The atoms were randomly inserted in cubic simulation boxes followed by 4 ps of annealing at T = 1500 K using AIMD simulations. NVT ensembles with Langevin thermostat and a time step of 1 fs were used for the simulations. During the annealing process, the atoms were allowed to freely rearrange. After annealing, the systems were quenched at a rate of 0.3 K/fs to T = 300 K using NPT ensemble. This was followed by 4 ps of NPT simulation at T = 300 K to allow for equilibration and 4 ps of NVT simulation for production.

The lithium intercalated amorphous silicon suboxide structures, *a*-Li_xSiO_y, were simulated by randomly adding lithium ions in the simulation box followed by 4 ps of NPT simulation for equilibration and 4 ps of NVT simulation for production. The lithium ions were added in four steps (x = 1, 2, 3, 4) until saturation. The compositions of the *a*-Li_xSiO_y structures are described in Table 1.

The DFT calculations were performed using *Vienna ab Initio Simulation Package* [14,15]. The Generalized Gradient Approximation (GGA) and Perdew–Wang 91 (PW91) functional were applied to represent the core electronic structure [16]. The interaction between valence and core electrons was described by the all electron frozen core, Projector Augmented Wave (PAW) method. All atoms were fully minimized with conjugate gradient method. We employed an energy cutoff of 400 eV and a k point mesh size of 2 × 2 × 2 in the Monkhorst–Pack scheme [17] for the Brilloin zone sampling, validated to be sufficient for the highly disordered *a*-Li_xSiO_y systems in a previous study [11].

Table 1
Compositions of the *a*-Li_xSiO_y structures.

System	# Li	# Si	# O
a-Si	0	30	0
a-LiSi	30	30	0
a-Li_2Si	60	30	0
a-Li_3Si	90	30	0
a-Li_4Si	120	30	0
a-$SiO_{0.1}$	0	30	3
a-$LiSiO_{0.1}$	30	30	3
a-$Li_2SiO_{0.1}$	60	30	3
a-$Li_3SiO_{0.1}$	90	30	3
a-$Li_4SiO_{0.1}$	120	30	3
a-$SiO_{0.2}$	0	30	6
a-$LiSiO_{0.2}$	30	30	6
a-$Li_2SiO_{0.2}$	60	30	6
a-$Li_3SiO_{0.2}$	90	30	6
a-$Li_4SiO_{0.2}$	120	30	6
a-$SiO_{0.3}$	0	30	9
a-$LiSiO_{0.3}$	30	30	9
a-$Li_2SiO_{0.3}$	60	30	9
a-$Li_3SiO_{0.3}$	90	30	9
a-$Li_4SiO_{0.3}$	120	30	9
a-$SiO_{0.4}$	0	30	12
a-$LiSiO_{0.4}$	30	30	12
a-$Li_2SiO_{0.4}$	60	30	12
a-$Li_3SiO_{0.4}$	90	30	12
a-$Li_4SiO_{0.4}$	120	30	12
a-$SiO_{0.5}$	0	30	15
a-$LiSiO_{0.5}$	30	30	15
a-$Li_2SiO_{0.5}$	60	30	15
a-$Li_3SiO_{0.5}$	90	30	15
a-$Li_4SiO_{0.5}$	120	30	15

3. Results and discussion

3.1. Analysis of the structure

Fig. 1 shows the different amorphous structures of Li_xSiO_y system for x = 0, 1, 2, 3, 4 and y = 0.5. It can be seen that the Li, Si and O atoms are well dispersed in the amorphous structures. A gradual disintegration of the initial $SiO_{0.5}$ structure (contacts between Si and O) is evident at increasingly higher level of Li atom insertion. Although many of the O atoms are surrounded by Li atoms, some are still interacting with Si atoms.

We note that the microscopic structure of silicon suboxide is complex and still under controversy. The experimental characterizations of silicon suboxide microstructures reveal that it can exist in both, homogenous and *a*-Si/*a*-SiO_2 nanocomposite forms [10]. The homogenous structure is stable under ambient conditions [10]. It is worthy to mention that *a*-Si/*a*-SiO_2 nanocomposite structures can be acquired through prolonged annealing of the initial homogenous form at high temperature which can lead to disproportionation of silicon suboxide into a mixture of *a*-Si and *a*-SiO_2 [18–22]. Other computational studies were devoted in understanding the complex behavior of silicon suboxide in microscopic details, for instance, the formation of Si nanocrystals in Si suboxide composite was studied by a Monte Carlo method [23]. Due to the complex nature of the nanocomposite structures, it is almost