



Lithiation-induced interfacial failure of electrode-collector: A first-principles study

Panpan Zhang^{a,b}, Zengsheng Ma^b, Yan Wang^c, Youlan Zou^b, Lizhong Sun^b, Chunsheng Lu^{a,*}

^a School of Civil and Mechanical Engineering, Curtin University, Perth, Western Australia, 6845, Australia

^b National – Provincial Laboratory of Special Function Thin Film Materials, and School of Materials Science and Engineering, Xiangtan University, Hunan, 411105, China

^c School of Information and Electronic Engineering, Hunan University of Science and Technology, Hunan, 411201, China

HIGHLIGHTS

- Lithiation severely weakens the $\text{Li}_x\text{Sn}/\text{Cu}$ interface strength with a reduction of $\sim 70\%$.
- Fracture of $\text{Li}_x\text{Sn}/\text{Cu}$ occurs near the interface region rather than at interface.
- The enhanced interface strength and deformation resistance can be realized on $\text{Cu}_x\text{Sn}/\text{Cu}$ interfaces.

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ABSTRACT

By using first-principles calculations, we investigate the interfacial failure between a lithiated Sn electrode and a Cu current collector for lithium-ion batteries. The results show that segregation of Li ions at the interfacial region leads to the transformation of interfacial bonding from Sn–Cu to Li–Cu bonds, and weak Li–Sn bonds near the interface region. This leads to the weakened interfacial strength upon lithiation and failure of most lithiated Sn/Cu interfaces within Li_xSn slabs. In addition, the formation of Cu_xSn alloys at interface could increase the interface strength and enhance the deformation resistance of electrode materials, which explains why Cu_xSn containing composite electrodes exhibits the excellent electrochemical performance.

1. Introduction

Although lithium-ion batteries (LIBs), as dominant energy storage devices, have been widely used in portable electronics and electric vehicles, current technologies cannot meet the rapidly growing demand for the high energy density and long cycle life [1]. Sn is considered as a promising candidate anode material for LIBs due to its high theoretical capacity of 994 mAh g^{-1} , about two and a half times of a conventional graphite anode [2]. However, application of Sn anode materials is restricted since they commonly experience a massive volume change ($\sim 300\%$) and a large stress during lithiation and delithiation processes. The large stress causes structural degradation of electrode materials, resulting in failure of LIBs [3,4].

To alleviate these problems, various nano-sized structures have been adopted to stabilize the capacity of Sn anodes, such as Sn nanowires, graphene nanosheets, carbon-fibers, and Sn@C nanoparticles [5–8]. Great advance has been made in the capacity and cycling stability of electrode materials, however, their electrochemical performance is still far from commercial requirements. This has stimulated

the research to clarify failure mechanisms of Sn anodes.

Microcracking and debonding are two main types of structural damage caused by the insertion of Li ions into active materials. Winter et al. [9] showed that the electrochemical lithiation of Sn caused surface cracks and local delamination from the Cu collector, which eventually led to loss of electronic contact. By using *in-situ* observation, Chao et al. [10] revealed that cracks appear in the lithiated layer of Sn particles during the first lithiation. Through investigating the electrochemical characteristic, cracking of Sn film during the first discharging was found [11]. In addition, cracking and debonding of amorphous Si from Cu-foil substrate were observed during electrochemical cycling [12]. Obviously, lithiation-induced microcracking and debonding of electrode materials present a challenge to the application of Sn anodes in high-capacity LIBs.

To address the structural damage during the lithiation process, Zhang et al. [13] discussed the layered structural configuration including active electrode film and current collector, which aided the optimal design of LIBs. Fang et al. [14] discovered that pre-strain greatly alleviated the diffusion-induced stresses of electrode film and

* Corresponding author.

E-mail addresses: zma@xtu.edu.cn (Z. Ma), C.Lu@curtin.edu.au (C. Lu).

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current collector, especially stress drop at the electrode-collector interface. Using the theory of diffusion-induced stress and the energy principle, analytical relations between the critical concentration of solute atoms and average damage size were established for the insertion-induced cracking and buckling in an elastic film [15]. Besides, it is shown that the formation of Cu_xSn intermetallic compound layers (Cu_6Sn_5 and Cu_3Sn) between Sn active materials and Cu current collectors could enhance the interface strength, which contributes to improved capacities and capacity retention [16–19]. A lot of Cu_6Sn_5 containing composites were explored as potential anodes for LIBs [20–22].

Previous microscopic investigations of Sn anodes were mainly focused on the failure mechanism of active materials during lithiation such as phase evolution [23,24], the change of mechanical properties [24–28], as well as the diffusion of Li ions in active materials [29–31]. However, to the best of our knowledge, there are few studies on the failure mechanism of electrode-collector interface at the atomic scale. In this paper, by using first-principles calculations, we investigate the lithiation-induced interfacial failure of Sn anodes, such as interface strength, fracture locations and the evolution of interfacial bonding. The effect of Cu_xSn alloys on interfacial mechanical properties is also discussed. It is expected that such a work can highlight the evolution of interfacial mechanical properties during lithiation, and further help to understand the role of lithiation and Cu_xSn alloys on the interfacial failure of electrode-collector.

2. Calculation methods and models

All calculations were performed by using the Vienna Ab initio Simulation Package (VASP) [32,33]. The generalized gradient approximation was adopted as the electron exchange-correction functional and the projected augmented wave method was applied to describe the ion-electron interaction [34]. The plane-wave energy cut-off of 380 eV and gamma centered k -meshes were used in calculations (see Table 1). The change of total energy of LiSn/Cu interface versus the plane-wave energy cutoff was given in Fig. S1. The convergence tolerance for electronic relaxation was 10^{-5} eV and the total energy was calculated by the tetrahedron method coupled with the Blöchl correction. Structural relaxation was carried out by using the conjugate gradient method until the Hellmann-Feynman forces on constituent atoms were less than 0.01 (bulk and surface) and 0.05 (interface) eV/Å, respectively. For bulk relaxation, the atom positions, volumes, and shapes were fully relaxed. Four kinds of crystal Li_xSn alloys (Li_2Sn_5 , LiSn, Li_5Sn_2 and Li_7Sn_2) and pure Sn were chosen to evaluate the lithiation effect on the interfacial properties of Sn anodes. As summarized in Table 1, the optimized lattice parameters are consistent with the experimental values [35–40].

Based on the optimized bulk structures and stable surfaces of Li_xSn (see Supporting Information), two kinds of interface models (vacuum and dense cells) were created by using the Virtual NanoLab-Atomistic ToolKit [41]. In vacuum cells, stable Li_xSn slabs were placed on Cu (111) slabs [42,43] with 15 Å vacuum added along the c axis of simulation cells, as shown in Fig. 1 and Table 2. For $\text{Li}_x\text{Sn}/\text{Cu}$ interfaces, there are three possible atomic stacking configurations, that is, the interfacial Sn or Li atom locates at top, bridge and vacancy sites of

interfacial Cu atoms. As an example, the three atomic stacking configurations of $\text{Li}_7\text{Sn}_2(001)/\text{Cu}(111)$ interface are illustrated in Fig. 2. The lattice mismatches for all interfaces are less than 5%. In calculations, atom positions were relaxed into the vacuum region above interface without changing the cell shape and volume. The optimum separations (~ 0.24 nm) of original structures were obtained by the full relaxation of interface supercells with different separations.

The LiSn/Cu dense cell is composed of alternate stacking of a LiSn slab and a Cu slab with fully periodic boundary conditions. No vacuum was added in the model, as shown in Fig. 1(f). Both atom positions and the cell length along the c -direction were optimized during the structural minimization. Failure of the interface was simulated by applying a uniaxial tensile strain along the c -axis of the dense cell while allowing structural relaxation along the other five strain components. All the internal freedoms of atoms were relaxed at each step. To ensure the continuous strain path, the initial position of each step was taken from the relaxed configuration of a previous strain step.

The interface strength was evaluated by the work of separation (W_{sep}), which is defined as

$$W_{\text{sep}} = (E_{\text{Li}_x\text{Sn-unrelax}} + E_{\text{Cu-unrelax}} - E_{\text{Li}_x\text{Sn}/\text{Cu}})/A_i \quad (1)$$

where $E_{\text{Li}_x\text{Sn}/\text{Cu}}$ is the total energy of a relaxed $\text{Li}_x\text{Sn}/\text{Cu}$ interface system, $E_{\text{Li}_x\text{Sn-unrelax}}$ and $E_{\text{Cu-unrelax}}$ refer to the total energies of isolated Li_xSn and Cu slabs in the same cell when one of them is kept and the other is replaced by vacuum, and A_i is the total interface area [44]. W_{sep} is the energy consumption per unit area in separating an interface into two fixed separate surfaces with the same atomic positions as the interface.

Then, each separate surface was relaxed into a free surface to obtain the adhesion energy W_{ad} , which is the energy gain per unit area to reversibly separate an interface into two free surfaces, neglecting plastic and diffusional degrees of freedom, that is

$$W_{\text{ad}} = (E_{\text{Li}_x\text{Sn-relax}} + E_{\text{Cu-relax}} - E_{\text{Li}_x\text{Sn}/\text{Cu}})/A_i \quad (2)$$

where $E_{\text{Li}_x\text{Sn-relax}}$ and $E_{\text{Cu-relax}}$ are the total energies of isolated Li_xSn and Cu slabs in the same cells after relaxation. All the surface calculations were conducted in the same supercell as that for interfacial calculations.

The work of decohesion (W_{dec}) is defined as the energy difference (per unit surface area) between the fractured system and the interface structure at a zero-stress state, namely

$$W_{\text{dec}} = (E_{\text{frac}} - E_0)/2A_s \quad (3)$$

where E_{frac} and E_0 are the total energies of the fractured and the zero-stress state $\text{Li}_x\text{Sn}/\text{Cu}$ interfaces, respectively. A_s is the corresponding surface area. W_{dec} can be used to confirm the fracture location of interface structures. If $W_{\text{dec}} > W_{\text{sep}}$, fracture occurs at the interface, otherwise, it is energetically more favourable to fracture within the Li_xSn slab [44].

3. Results and discussion

3.1. Interface strength of $\text{Li}_x\text{Sn}/\text{Cu}$ interfaces

As listed in Table 3, $\text{Li}_x\text{Sn}/\text{Cu}$ interfaces demonstrate almost the

Table 1

Lattice constants (in the unit of Å) and k -points used in bulk calculations, where experimental values are listed in parentheses [35–40].

Phase	x	$y = x/(1 + x)$	a	b	c	Volume	k -points
β -Sn	0.0	0.00	5.941 (5.831)	5.941 (5.831)	3.208 (3.184)	113.21	$9 \times 9 \times 16$
Li_2Sn_5	0.4	0.29	10.386 (10.274)	10.386 (10.274)	3.141 (3.125)	338.80	$5 \times 5 \times 16$
LiSn	1.0	0.50	5.155 (5.172)	7.765 (7.742)	3.236 (3.182)	125.15	$10 \times 7 \times 16$
Li_5Sn_2	2.5	0.71	4.722 (4.740)	4.722 (4.740)	19.822 (19.833)	382.80	$8 \times 8 \times 2$
Li_7Sn_2	3.5	0.78	9.811 (9.802)	13.844 (13.803)	4.713 (4.752)	640.06	$3 \times 2 \times 7$
Cu	–	–	3.631 (3.615)	3.631 (3.615)	3.631 (3.615)	47.87	$13 \times 13 \times 13$

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