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Nanoscale silicon-based actuators with extremely large actuation strain and extremely low driving voltage

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ABSTRACT

The coupling between lithiation reaction of silicon and the considerable volume change has been widely recognized as an adverse effect which hinders the practical application of silicon-based lithium-ion batteries. Here we theoretically demonstrate a novel class of nanoscale electrochemically-driven silicon actuators, in virtue of the "unfavorable" gigantic volume expansion engendered by lithiation. Two representative design prototypes are reported, namely, a nano-sized flat-film silicon actuator and a nanowire silicon actuator. Our thermodynamic analysis establishes the operation condition of the actuators by identifying the electrochemical driving force and mechanical resistance due to lithiation-induced stress. We show that the nano-actuator exhibits an extremely low driving voltage about 1 V and an extremely high strain of actuation up to 300%, which goes far beyond the features of most common actuator materials. Given a mechanical load, the flat-film silicon actuator features a constant actuation strain and the nanowire actuator can provide tunable actuation strain. The results from the study offer quantitative guidance to the design of the novel silicon-based nano-actuators.

Silicon has been highlighted as a promising alternative to conventional graphite, owing to its superior specific capacity which is one order of magnitude higher than that of graphite anodes. The high theoretical capacity arises from the ability to host substantially more lithium than graphite. Nevertheless, the insertion of a large number of lithium atoms leads to considerable volume expansion (about 300%) of the silicon, which causes structural destruction of the electrode and severe capacity fading, thereby hindering the practical application of silicon anode in commercial batteries [1,2]. In order to put silicon into use as a practical anode, tremendous efforts have been devoted to alleviating the mechanical failure of silicon anodes induced by the excessive volume expansion, typically by nano-structuring [2], nano-compositing [3,4], designing microporous structures [5,6], or exploiting novel binders to hold silicon particles together [7]. Now that mechanical degradation of Si due to the huge volumetric change has been mitigated to varying degrees of success with the aforementioned strategies.

Although a significant amount of research has been performed with the goal of addressing the adverse effect of lithiation-induced expansion, few efforts have been made to instead harness the gigantic lithiation-induced strain to provide useful functions. For its first time, Lang et al. demonstrated a macroscale actuator based on a LiFePO4/Si full cell which can drive a large mechanical load with an output strain about 1% [8]. Macroscopic actuators based on Li-reactive materials beyond silicon, such as germanium, were also reported [9]. In addition to the lithiation-enabled actuator, researchers also developed generators based on electrode materials by taking advantage of the stress-regulated lithiation kinetics [10,11]. Kim et al. developed a new class of energy-harvesting device comprised of two partially lithiated silicon films sandwiching an electrolyte [11]. Through stress–voltage coupling, the asymmetric stress state engendered by bending gives rise to a chemical potential difference which drives the charge carriers to shuttle between the two electrodes, thereby converting mechanical energy into electrical energy [12].

The functionality of the abovementioned actuator and generator arises from the lithiation-induced strain and the stress-mediated lithiation, respectively. Herein, we theoretically demonstrate a new type of nanoscale actuator based on the unique two-phase lithiation mechanism of nano-sized silicon [13–16], by harnessing the intimate coupling between lithiation and mechanics. Two prototypes are presented, i.e., a flat-film silicon actuator (Fig. 1a) and a nanowire silicon actuator (Fig. 1c). Our analysis predicts that driven by an extremely low input voltage below 1 V, the nanoscale actuators based on lithiation of silicon exhibit an extremely high actuation strain up to 300% and an extremely large actuation stress beyond 1 GPa, which is superior to common electroactive actuator materials. Moreover, the fully coupled lithiation kinetics and mechanical stress endow the

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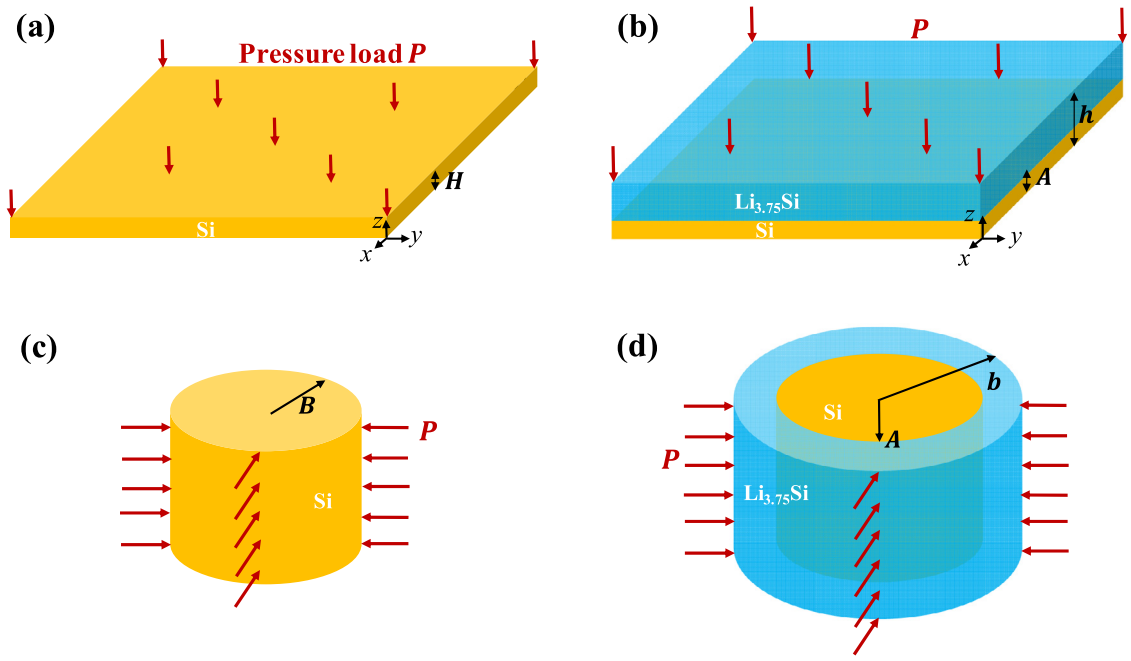

Fig. 1. Schematics of the conceptual lithiated-silicon-based actuator. (a) The initial flat-film silicon actuator of thickness H. A uniform pressure P is imposed to the top surface of the film to represent the mechanical load to be actuated. (b) The working principle of the nanoscale flat-film actuator. Upon lithiation, lithium ions are inserted into the film through its top surface, the silicon film becomes a double-layer structure consisting of a top lithiated layer (blue) and a bottom pristine layer (yellow) which are separated by an interface (namely, the reaction front) at $z = A$. The lithiated phase thickens continuously as the reaction front moves downwards, thereby lifting the mechanical loads. (c) The initial configuration of the nanowire silicon actuator of radius B. (d) The working principle of the nanowire actuator. Lithium ions migrate into the nanowire through its lateral surface and the reaction front of $r = A$ moves towards the center of the nanowire, which causes the shrinkage of the remaining silicon core (yellow) and the expansion of the lithiated shell (blue), thus pushing out the mechanical loads. The current outer radius of the actuator is given by b. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

nanowire actuator with tunable actuation strain, which has not been achieved by the macroscale actuators based on Li–Si alloy.

To illustrate essential ideas, we sketch the schematics of the two types of nanoscale actuators in Fig. 1, namely, a flat silicon film (Fig. 1a and c) and a silicon nanowire (Fig. 1b and d) subjected to lithiation reaction. A uniform pressure P is applied to the top surface of the film and the lateral surface of the nanowire, respectively, to model the dead loads that to be displaced by the nano-actuators. We take the flat-silicon film (Fig. 1a) as an example to elucidate the working principle of the silicon-based actuators. It is important to recognize that the actuator design presented in the current study is based on the lithiation of pristine silicon, a process intrinsically different than the lithiation of post-lithiated alloys (namely, silicon or germanium that already undergoes various degrees of lithiation and delithiation). Consequently, the actuation mechanism of the nanoscale actuator proposed here is governed by the reaction kinetics between lithium and fresh silicon, instead of the diffusion kinetics of lithium in the lithiated phase. Under the operation condition, lithium ions enter the flat silicon film through its top surface, thus the film becomes a bilayer structure composed of a top lithiated layer ($Li_{3.75}Si$, blue in Fig. 1) and a bottom pristine silicon layer (yellow) which are separated by a phase interface, as illustrated in Fig. 1b. Lithium atoms continuously diffuse to the interface and react with fresh silicon, transforming the silicon phase to the lithiated silicon phase and generating significant volume expansion. As a consequence, the phase interface moves downwards and the lithiated layer thickens drastically, thereby driving large actuation of the mechanical loads. The actuation goes on until the lithiation reaction halts. (To be consistent with the nomenclature adopted in the reference [17], we will refer to the phase interface as the reaction front hereafter since the lithiation reaction occurs on the interface.)

We next quantitatively identify the operation condition of the silicon-based nano-actuators. As analyzed above, the "engine" of the actuator is the lithiation reaction taking place at the reaction front which converts lithium ions (namely, the "fuel" for the engine), electrons, and silicon atoms into the $Li_{3.75}Si$ phase and simultaneously generates actuation strain. The lithiation reaction can be described by the chemical reaction equation that

$$\mathrm{Li}^+ + \mathrm{e}^- + \frac{1}{3.75}\mathrm{Si} = \frac{1}{3.75}\mathrm{Li}_{3.75}\mathrm{Si} \tag{1}$$

The change in free energy associated with the reaction (i.e., the free energy of the products minus that of the reactants) can be identified as $\Delta G = \Delta G_{chem} + \Delta G_{elec} + \Delta G_{mech}$. ΔG_{chem} denotes the change in free energy associated with the chemical reaction when both applied voltage and stress vanish. $\Delta G_{elec} = -e\Phi$ is the energy change due to the work done by the voltage, where Φ is the voltage applied to the actuator (i.e., the bias voltage between the silicon and the lithium source) and e the elementary charge. It should be pointed out that experimental studies have evidenced that the value of applied voltage Φ remains a constant under both potentiostatic condition and galvanostatic condition since the lithiation of nano-sized silicon is a reaction limited process [18]. ΔG_{mech} represents the contribution of lithiation-induced stress to the free energy change.

According to the definition of ΔG, a negative ΔG triggers the reaction, which starts the "engine" of the actuator and drives it to lift loads, while a non-negative ΔG arrests the reaction and shut down the "engine" of the actuator. That is to say, the actuator functions when $\Delta G_{mech} < e\phi - \Delta G_{chem}$, but the actuator loses power if $\Delta G_{mech} \geq e\phi - \Delta G_{chem}$. The value of $e\Phi$ is dictated by the applied voltage Φ and always takes a positive value. It has been reported that ΔG_{chem} is intrinsically negative, for instance, $\Delta G_{chem} = -0.18$ eV for $Li_{2.1}Si$ [19]. It follows that the term of $e\phi - \Delta G_{chem}$ remains a constant once an external voltage is applied.