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Review

Silicon-based materials as high capacity anodes for next generation lithium ion batteries

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HIGHLIGHTS

- The paper reviewed the merits of silicon-based anodes in lithium ion batteries.
- The mechanisms were discussed from in-situ TEM and first-principles simulation.
- The challenges faced in silicon-based anodes were analyzed and forecast.

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ABSTRACT

Silicon (Si)-based materials have the highest capacity among the investigated anode materials and have been recognized as one of the most promising materials for lithium-ion batteries. However, it is still a significant challenge to obtain good performance for practical applications due to the huge volume change during the electrochemical process. To date, the most successful strategy is to introduce other components into Si to form composite or alloy materials. In this review, the recent progress in Si-based materials utilized in lithium-ion batteries is reviewed in terms of composite systems, nano-structure designs, material synthesis methods, and electrochemical performances. The merits and disadvantages of different Si-based materials, the understanding of the mechanisms behind the performance enhancement as well as the challenges faced in Si anodes are also discussed. We are trying to present a full scope of the Si-based materials, and help understand and design future structures of Si anodes in lithium-ion batteries.

1. Introduction

Among all investigated anode materials, silicon (Si) has a theoretical capacity of 3590 mAh g^{-1} (almost ten times higher than that of graphite) based on the fully alloyed form of $Li_{15}Si_4$ at room temperature (at high temperature $Li_{22}Si_4$ can be reached, giving a capacity of 4200 mAh g^{-1}), placing it on top of all other anode materials [1–3]. In addition, Si anodes show moderate working potential (~0.5 V vs. Li/Li^+) [4], which, in contrast to graphite anodes (~0.05 V vs. Li), avoid the safety concern of lithium deposition upon cell overcharge as well as avert the energy penalty of battery cells assembled with the $Li_4Ti_5O_{12}$ anodes (1.5 V vs. Li/Li^+) [5]. Fig. 1 showed a schematic of a lithium battery with a Si anode and a lithium metal oxide (LiM_xO_y) intercalation cathode [3]. However, the large number of lithium ion insertion/extraction results in huge volume change (~370% assuming final alloy of $Li_{15}Si_4$), which leads to structural pulverization and electrical disconnection between the active materials and the current collector, and finally fast capacity fading [2]. To circumvent these problems, tremendous efforts have been attempted, including methods from physical to chemical, from inorganic to organic. Among them the most successful strategy is to incorporate other components into Si materials, such as polymers, carbon, and metals. Significant progress and promising results have been achieved based on these composites. The material designs and performance results will be summarized and discussed in the following sections.

Failure of the Si anodes is mainly caused by the large volume expansion/contraction during lithium insertion/extraction because the intermetallics of Li/Si have much greater molar volume than the nanostructure Si phase, as shown in Fig. 2 [6]. Large stresses

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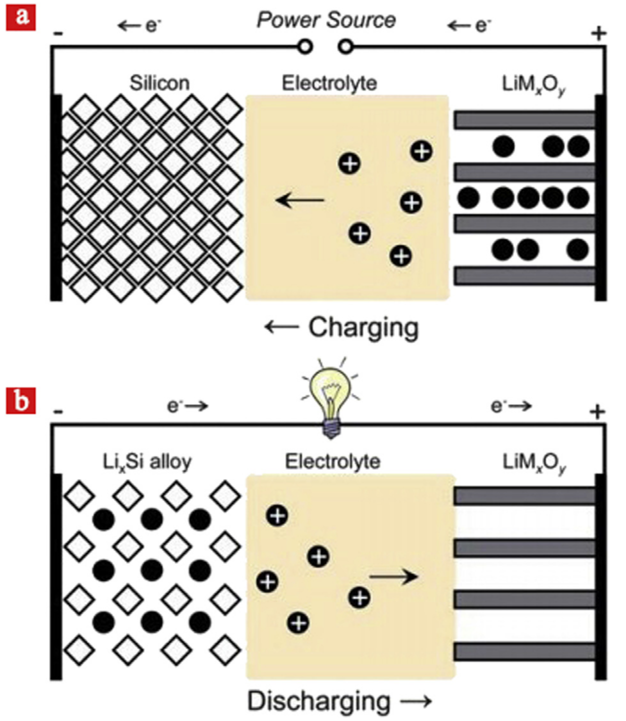

Fig. 1. Schematic of a lithium battery containing a Si anode and lithium metal oxide cathode during (a) charging and (b) discharging [3].

induced by the repetitive volume expansion and contraction can cause cracking and pulverization of the Si anodes, which leads to loss of electrical contact and eventual capacity fading [5,7–9] as shown in Fig. 3.

The behavior of lithiation-induced deformation and stress has been extensively studied in recent years. On the basis of theoretical calculation, several groups have investigated the lithium-insertion-induced swelling and stress and proposed or predicted the results in mechanical failure. For instance, Christensen and Newman calculated swelling and stress [10,11], Sastry and co-workers simulated the stress generation during lithiation under galvanostatic control [12], Cheng and coworkers calculated the strain energy under both potentiostatic and galvanostatic operations in spherical particles [13,14]. Lithiation-induced stress in Si has also been calculated [15,16]. Several recent papers have reported lithiation-induced fracture by applying electrochemical mechanics [17–19].

The large volume changes also cause significant challenges on the morphology and integrity of the entire electrodes. The drastic electrode morphology change can influence the integrity of the electrodes and further result in the capacity fading. The electrode cracking and peeling-off have been observed by several research groups. Kim et al. investigated the variations in volume and density as a function of Li content [20]. They found that when the Li content was sufficiently high, alloying between Li and silicon was energetically favorable as evidenced by the negative mixing enthalpy; the alloy was most stable around 70 atom% Li in the crystalline phase and 70 ± 5 atom% Li in the amorphous phase. Many other researchers also studied the volume expansion and received similar results [21–23]. The previous studies have shown that the large deformation of Si electrodes during electrochemical process could be alleviated by plastic flow [24]. The electrode morphology and integrity are especially relevant to the geometries of the nano-structured electrodes. Motivated by this phenomenon, Zhao et al. elucidated the plastic deformation in lithiated Si under uniaxial tension [23]. The microscopic mechanism of large plastic deformation is attributed to continuous lithium-assisted breaking and reforming of Si–Si bonds and the creation of nano-pores.

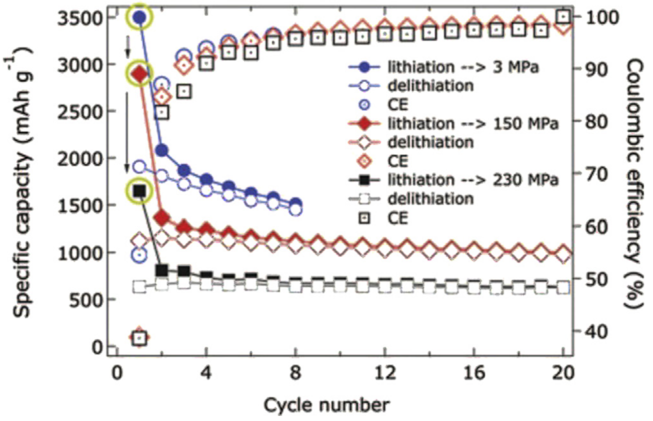

Fig. 3. Electrochemical performance and CE of solid-state nano-Si composite anodes cycled at a rate of C/20 under compressive pressures of 3 (blue), 150 (red) and 230 (black) MPa [9]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Solid-electrolyte interphase (SEI) film that resulted from the decomposition of electrolytes is another important factor in the battery performance, which leads to irreversible capacity loss. The formation of this passivating SEI film on the Si surface has been confirmed by high resolution transmission electron microscopy (HRTEM), Fourier Transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) [25–27]. The SEI stability at the interface between Si and the liquid electrolyte is a critical factor in cycle life and coulombic efficiency. For example, Arie et al. investigated the electrochemical performance of phosphorus- and boron-doped nanostructure Si thin-film anodes [28]. They found that the doped Si showed much better cycling stability and higher capacity than the un-doped Si films, which is attributed to the formation of stable SEI layer on the surface of the doped electrodes.

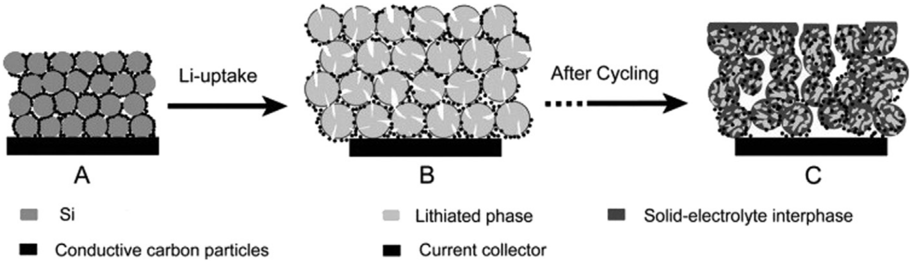

Fig. 2. Structure demolition of Si anode during lithium insertion [6].