



Short communication

## Simple annealing process for performance improvement of silicon anode based on polyvinylidene fluoride binder

YuHong Xu<sup>a</sup>, GePing Yin<sup>a,b,\*</sup>, YuLin Ma<sup>a</sup>, PengJian Zuo<sup>a</sup>, XinQun Cheng<sup>a</sup><sup>a</sup> School of Chemical Engineering and Technology, Harbin Institute of Technology, No. 92, West Da-Zhi Street, Harbin 150001, China<sup>b</sup> State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150001, China

## ARTICLE INFO

## Article history:

Received 3 July 2009

Received in revised form

11 September 2009

Accepted 15 October 2009

Available online 23 October 2009

## Keywords:

Li-ion battery

Silicon anode

Polyvinylidene fluoride binder

Annealing

Peel test

## ABSTRACT

An annealing method has been reported for silicon anode based on polyvinylidene fluoride (PVDF) binder. High initial coulombic efficiency of 75.6% and a stable reversible capacity of 715.6 mAh g<sup>-1</sup> for 50 cycles have been obtained after annealing process. Such improvements are attributed to the enhanced cohesive ability of PVDF and the compact morphology of the electrode reconstructed by annealing, which improves the electronic contacts of silicon particles and stabilizes the electrode structure effectively. It is demonstrated that such annealing method is very economic and effective for performance improvement of silicon anode.

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### 1. Introduction

Li-ion batteries are promising power sources for portable devices and the urgent needs to get rid of the dependence on petrol oil also make them hot topics in electronic vehicles (EV). However, the commercialized LiCoO<sub>2</sub>/graphite system cannot satisfy the demands of EV due to the limited capacity of graphite (372 mAh g<sup>-1</sup>) and potential anode materials possessing higher capacity are needed. Silicon is the potential candidate with the highest capacity of 4200 mAh g<sup>-1</sup>, but the severe volume changes make it unavailable in practice. Many efforts have been made to solve this problem, such as incorporating inactive/active elements as cushions against volume changes [1–6], or roughing surface of current collector to bond the collector and active material tightly [7]. Some of these methods are worked effectively, but relative complex and costly methods are adopted. Concerning the binder, CMC (carboxyl methyl cellulose) has been applied successfully in industrial production of carbonaceous material. Recently, it is also proposed as a promising binder for silicon anode [8,9]. However, many published literatures demonstrate that PVDF (polyvinylidene fluoride) is still used widely by many research institutes in studies of silicon anode. Consequently, it is still of significance to improve the properties of silicon-based anode based on PVDF binder.

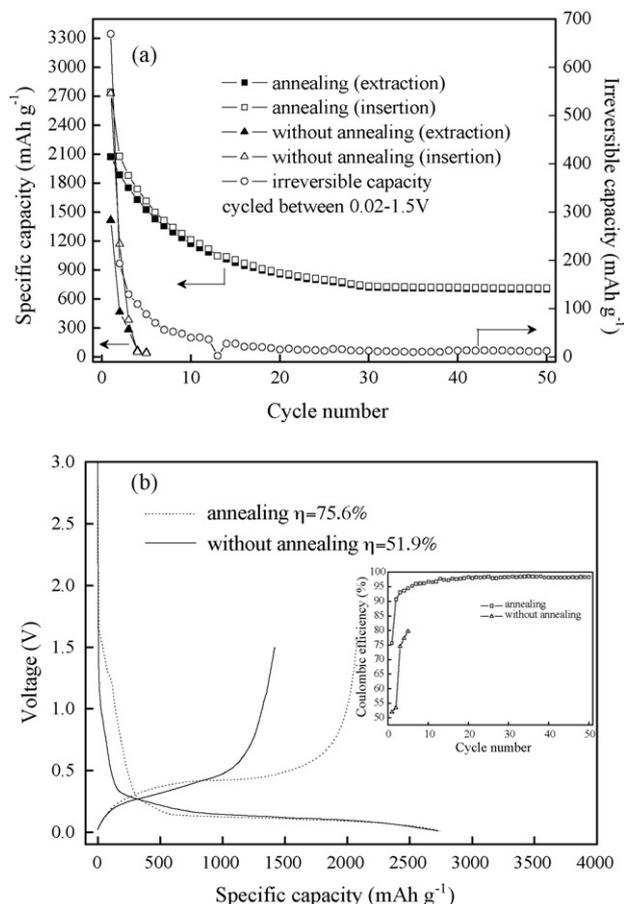
In this study, we reported an annealing method following the slurry casting for silicon anode and investigated the possible mechanism for performance improvement originated from such annealing process.

### 2. Experiments

Silicon powder (JiNan YinFeng, China, –120 mesh, >99.5%) was purchased and ball milled for 48 h under the protection of argon gas for usage. The weight ratio of stainless steel ball to silicon powder was 10:1. The ball milled silicon has a particle size of 0.2–2 μm. The electrodes were prepared by casting slurry containing 60 wt% silicon, 16 wt% acetylene black (AB) and 24 wt% PVDF on copper foil and dried at 120 °C for 10 h under vacuum. The electrodes were punched into disks (Ø = 14 mm) and pressed as the research electrodes by hydraulic press at the pressure of 10 MPa. The electrode material loading is 0.6499 mg cm<sup>-2</sup> (including silicon, AB and PVDF). Some of these electrodes further experienced an annealing process at 230 °C for 3 h under argon gas. The cells were assembled with coin cells in argon-filled glove box, using lithium metal as counter electrode, 1 mol L<sup>-1</sup> LiPF<sub>6</sub> (EC/EMC/DMC, 1:1:1, v/v/v) as electrolyte and Celgard2400 membrane as separator.

The morphologies of the electrodes were characterized with scanning electronic microscopy (SEM, Hitachi S-4700). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with electrochemical analyzer (CHI604b). CV measurement is performed at the scan rate of 0.1 mV s<sup>-1</sup> within

\* Corresponding author. Tel.: +86 451 86413707; fax: +86 451 86413707.  
E-mail addresses: [yhxhit@163.com](mailto:yhxhit@163.com) (Y. Xu), [yingphit@hit.edu.cn](mailto:yingphit@hit.edu.cn) (G. Yin).



**Fig. 1.** (a) Cyclability and (b) initial voltage profiles of bulk silicon anode with/without annealing process. (The cells are cycled between 0.02 and 1.5 V.)

the voltage range of 0–1.5 V. Galvanostatic charge (lithium extraction)/discharge (lithium insertion) was conducted with battery test system at the current of 50 mA g<sup>-1</sup> within voltage range of 0.02–1.5 V. EIS is measured after 5 charge/discharge cycles at the open circuit voltage at the charged state. The applied amplitude voltage is 5 mV with the frequency of 10<sup>-2</sup>–10<sup>5</sup> Hz. All the capacities are calculated based on the weight of silicon.

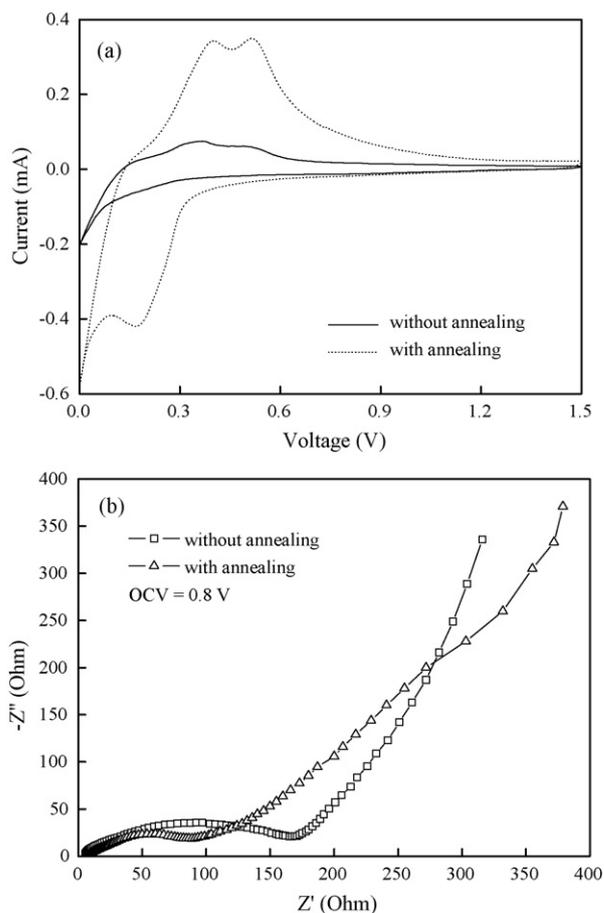
### 3. Results and discussion

Fig. 1(a) and (b) shows the cyclabilities and the initial voltage profiles of silicon anode with/without annealing process. The irreversible capacity and coulombic efficiency over the whole cycles are also present in Fig. 1(a) and (b). The non-annealed anode exhibits the initial reversible capacity of 1416.5 mAh g<sup>-1</sup> but decays sharply within 5 cycles. For annealed anode, the cyclability is improved remarkably and the initial reversible capacity of 2073.3 mAh g<sup>-1</sup> is obtained. After 50 cycles, the annealed anode still remains the stable reversible capacity of 700.6 mAh g<sup>-1</sup>, indicating much better cycling performance originated from annealing process. The irreversible capacity of the annealed electrode shows that the annealed electrode exhibits a large irreversible capacity of 669.3 mAh g<sup>-1</sup> at the first cycle. But after 35 cycles, the irreversible capacity is decreased to around 10 mAh g<sup>-1</sup> and kept to 50 cycles.

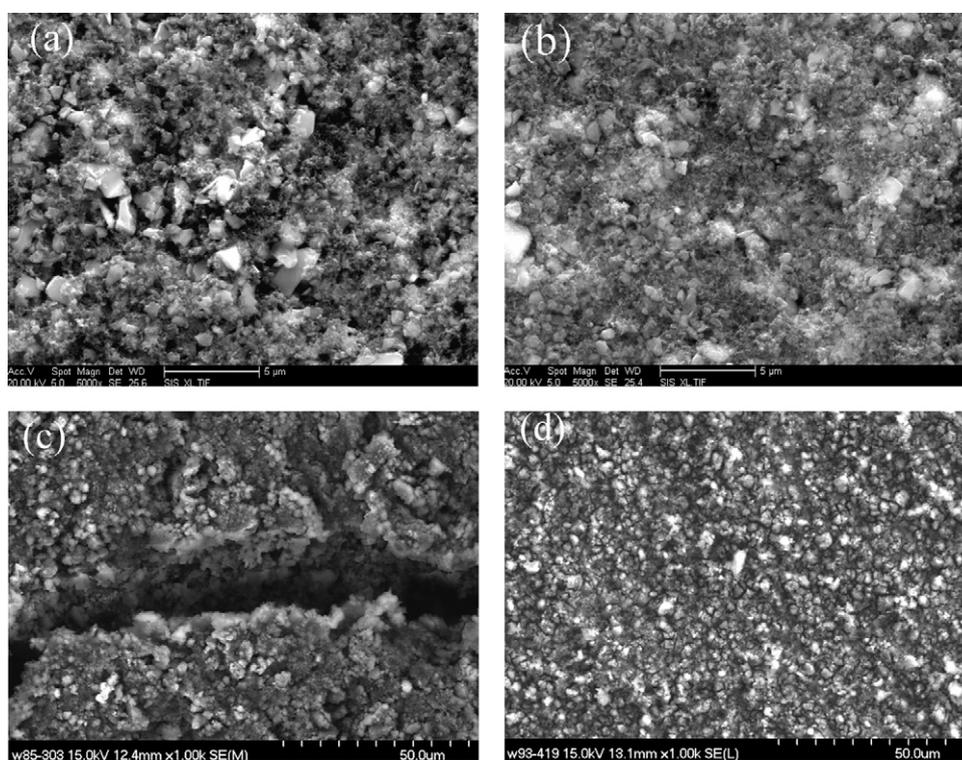
Concerning the initial voltage profiles, the curves are very similar to each other no matter the electrode is annealed or not, which means that the annealing process does not change the lithium insertion/extraction mechanism. Both the non-annealed and annealed electrodes exhibit the similar discharge capacities

of 2728.2 and 2742.6 mAh g<sup>-1</sup>, demonstrating that the annealing process has little effect on behaviors of lithium insertion. However, the lithium extraction is affected distinctly and the coulombic efficiency (η) is increased from 51.9% (non-annealed electrode) to 75.6% (annealed electrode). Seen from the inset in Fig. 1(b), the coulombic efficiency of non-annealed electrode is below 80% within 5 cycles. However, the annealed electrode shows a high efficiency of 95% after 5 cycles and above 98% in the subsequent cycles. It is known that the lithium insertion will bring huge volume expansion and the silicon particle will crack and lose electronic contacts. But here it seems that the annealing process has suppressed the volume expansion and kept the particles together tightly. To acknowledge of us, such high efficiency is rarely reported for silicon anode with PVDF as binder.

Fig. 2(a) shows the CV curves of anode with/without annealing process after initial charge/discharge cycle. The values of current peaks for annealed electrode are 3–4 times larger than that of non-annealed electrode, demonstrating much higher electrochemical activity after annealing process. Concretely, a cathodic peak corresponding to Li–Si alloying appears around 0.17 V and two anodic peaks corresponding to Li–Si dealloying are present around 0.4 and 0.5 V. However, the corresponding cathodic/anodic peaks are not present obviously for non-annealed electrode, indicating that less reversible lithium is available after one lithium insertion/extraction cycle. Nyquist plots (measured after 5 charge/discharge cycles at the charged state) in Fig. 2(b) further demonstrate that charge transfer impedance is reduced remarkably after annealing, which means that the electronic contacts of annealed anode are much better than that of non-annealed anode and the electrons are able



**Fig. 2.** (a) CV and (b) Nyquist plots of silicon anode with/without annealing process (at 0.8 V of charged state).



**Fig. 3.** SEM images of anode electrodes: (a) fresh electrode without annealing process; (b) fresh electrode with annealing process; (c) cycled electrode without annealing process; (d) cycled electrode with annealing process.

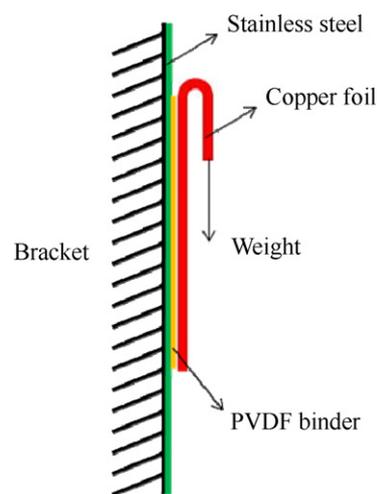
to move fluently. These further confirm that the volume change is restrained effectively after annealing and the silicon particles are interconnected tightly.

Fig. 3(a) and (b) shows the morphologies of fresh electrode with/without annealing process. Non-annealed electrode displays the incompact and porous structure. Large irregular silicon particles with sharp edges and smooth surface are exposed and isolated without interconnected, which tends to be pulverized easily and deviated from the network of conductive agent/binder, finally losing electric contacts by dynamical changes of lithium insertion/extraction. The melting point of PVDF is around  $170^{\circ}\text{C}$  and annealing process performed above this temperature will make PVDF melt, which will creep dynamically inside of electrode matrix and fill the gaps between particles, interconnecting the isolated particles and reconstructing the morphologies. As is seen, morphology of annealed electrode becomes more compact and large isolated silicon particles are inlaid in electrode matrix. In this case, the volume changes of the inlaid silicon will be suppressed effectively by electrode matrix itself without introducing any other external elements. Also, the inlaid silicon particles can keep better electric contacts via networks of conductive agent/binder than that of non-annealed electrode, which is favorable for electrochemical improvements.

Generally speaking, proper porous structure is desired for electrode, which will give out more effective reaction sites and absorb more electrolytes to promote the electrochemical activity. For silicon, however, due to the huge volume change, the internal stress from the volume change will reduce the stability of the electrode structure. Thus, if the morphology is incompact, such stress-destruction effect will be exacerbated and there are not enough buffers against the volume changes, finally destroying the electrode structure. Consequently, compact morphology with silicon particles inlaid in electrode matrix is necessary for restraining volume changes and keeping the stability of electrode structure.

After repeated lithium insertion/extraction cycles, the non-annealed electrode in Fig. 3(c) is severely destroyed and the electrode is cracked heavily. A huge ravine with the width of  $20\ \mu\text{m}$  is present. Instead, the annealed electrode in Fig. 3(d) affords the repeated lithium insertion/extraction effectively and keeps the integrity of the electrode structure.

Usually, binder plays the role of bonding particles or bonding the current collector and the coated active material, so the cohesive ability of binder is critical for maintaining the stability of the electrode matrix. Fig. 4 demonstrates the sketch of peel test to evaluate the cohesive ability of PVDF binder with/without annealing. The copper foil ( $15\ \text{mm} \times 60\ \text{mm}$ ) was stick to stainless steel (SS) slice by PVDF with same amounts and annealed at  $230^{\circ}\text{C}$  for 3 h, then



**Fig. 4.** Sketch of peel test for PVDF binder. (green: stainless steel slice; yellow: PVDF binder; red: copper foil) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

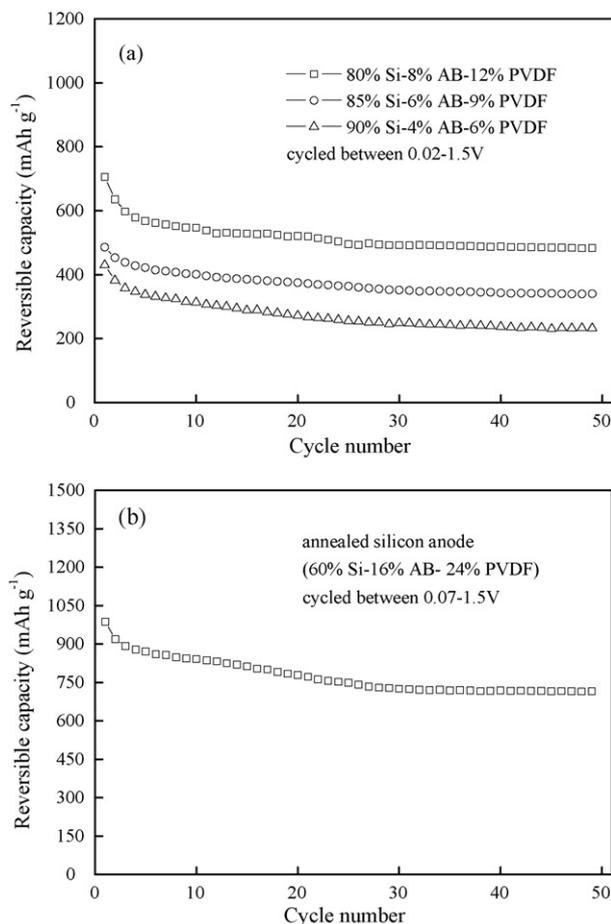


Fig. 5. Cyclability of silicon anode (a) with different silicon amounts and (b) with lower cutoff voltage of 0.07 V.

the SS was fixed on bracket. Afterwards, weights were added to the free end of the copper foil to draw it downwards. The weights were added gradually via weight set until the copper foil was peeled off the SS totally. The smaller the weight is, the weaker the cohesive ability of PVDF is. In non-annealed case, the final weight is 120 g, which is smaller than the 200 g for annealed case. Therefore, the peel test indicates that annealing intensifies the cohesive ability of PVDF. That also means indirectly that the cohesion of current collector/active material or particles/particles is enhanced greatly after annealing process, which will further restrain the volume change and stabilize the electrode structure.

Published literatures [10,11] have reported that silicon electrode with small amount of silicon and large amount of conductive additive can improve the cyclability to a great extent. Because the relative low silicon amount (60%) is used in above electrode, whether the improved cyclability is really brought by annealing should be further confirmed by using higher silicon amount. We further investigated the cyclability of annealed silicon anode with higher silicon amount (80% Si–8% AB–12% PVDF, 85% Si–6% AB–9% PVDF, 90% Si–4% AB–6% PVDF) in Fig. 5(a). As is seen, the overall capacities are decreased as the silicon amount is increased from 60% to 90%, which is in agreement with the results of Refs. [10,11]. However, all of the three electrodes show much better cyclability and retention than the non-annealed electrode in Fig. 1(a). A stable reversible capacity of 483.2, 340.6 and 232.7 mAh g<sup>-1</sup> is exhibited for electrode of 80% Si, 85% Si and 90% Si, respectively. This result confirms that our annealing method indeed improves the stability of silicon anode no matter the silicon amount or AB amount is small or large.

Fig. 5(b) investigates the effect of lower cutoff voltage on cyclability of annealed electrode (60% Si is used) and the cell is cycled between 0.07 and 1.5 V. Compared with the electrode cycled between 0.02 and 1.5 V in Fig. 1(a), the cell cycled between 0.07 and 1.5 V exhibits enhanced capacity retention and stable capacity of 715.6 mAh g<sup>-1</sup> is maintained for 50 cycles. This improvement is attributed to the avoiding of crystal Li<sub>15</sub>Si<sub>4</sub>, which is believed to form below 50 mV (vs. Li<sup>+</sup>/Li) and has negative effect on stability of silicon electrode.

To acknowledgement of us, our annealed silicon anode shows an attractive performance compared with others' works based on PVDF binder. Compared with the performance of silicon anode using CMC binder, our results are still not so good due to the intrinsic difference between two binders. For example, Dahn's group [12] obtained a high capacity of 1100 mAh g<sup>-1</sup> for 70 cycles with a lower cutoff potential of 0.170 V (vs. Li<sup>+</sup>/Li) by using CMC binder for silicon electrode. In spite of that, we think that our annealing method for PVDF binder system still owns the practicability for people who still use PVDF in their scientific investigations.

Based on the above analysis, we can propose a possible mechanism for performance improvement of annealing electrode as follows. For non-annealing electrode, during lithium insertion, the crystal silicon alloys with lithium and the volume is expanded to ~300% at lower voltage. During lithium extraction, the expanded silicon host is shrunked again. Such expansion/shrinkage will bring the cracking of silicon particles, even the peeling of active material from current collector. In this condition, the electrons paths are cut off at the cracks and the local electrochemical reactions are hindered, or the electrons cannot transfer from active material to current collector due to the peeling of active material, which further interrupt the electrochemical reaction. The cracked electrode structure finally results in the poor electrochemical performance. However, for annealed silicon anode, the electrode is more compact and silicon particles are enveloped or interconnected tightly by network of AB/PVDF, which possess high electronic contacts than non-annealed electrode. As the lithium insertion/extraction is repeated, although the volume change of silicon host is inevitable, the intensified cohesive ability of binder always maintains the better electronic contacts between active material and current collector, which guarantees the effective paths for electron transfer. Likewise, the compact electrode morphology not only envelops the silicon particles inside electrode matrix but also interconnects the particles and AB/PVDF network tightly, which will suppress the volume change to a great extent and make good electronic contacts between particles.

It is worth mentioning that because of the universality of the PVDF binder and the non-specific limiting condition for such annealing method, we believe such method can be extended to other alloy anodes that possess the same volume-change problems as silicon and the related researches are underway in our labs.

#### 4. Conclusions

In summary, an annealing process was reported for improvement of silicon anode. It is demonstrated that the annealing process enhances the cohesive ability of PVDF binder and changes the morphologies of electrode to be compact, which are supposed to suppress the volume changes of silicon and stabilize the electrode structure effectively.

#### Acknowledgements

The authors would like to thank the anonymous reviewers and the financial support from the Natural Science Foundation of China (No. 20673032).

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