



Role of polymeric binders on mechanical behavior and cracking resistance of silicon composite electrodes during electrochemical cycling

Dawei Li^{a,b}, Yikai Wang^b, Jiazhi Hu^b, Bo Lu^a, Dingying Dang^b, Junqian Zhang^{c,d,e,*}, Yang-Tse Cheng^{b,**}

^a Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China

^b Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

^c Department of Mechanics, Shanghai University, Shanghai 200444, China

^d Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai 200072, China

^e Materials Genome Institute, Shanghai University, Shanghai 200444, China

HIGHLIGHTS

- Role of binders on deformation and cracking of Si composite electrodes is explored.
- Curvature of Si/SA electrodes is larger than that of electrodes of Nafion and PVDF binders.
- Modulus of composites decreases not only during lithiation but also during delithiation.
- Composite modulus with sodium alginate binder is the highest, the PVDF the lowest.
- Cracking resistance of composite electrodes with SA and Nafion is higher than that with PVDF.

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ABSTRACT

This work focuses on understanding the role of various binders, including sodium alginate (SA), Nafion, and polyvinylidene fluoride (PVDF), on the mechanical behavior and cracking resistance of silicon composite electrodes during electrochemical cycling. *In situ* curvature measurement of bilayer electrodes, consisting of a silicon-binder-carbon black composite layer on a copper foil, is used to determine the effects of binders on bending deformation, elastic modulus, and stress on the composite electrodes. It is found that the lithiation induced curvature and the modulus of the silicon/SA electrodes are larger than those of electrodes with Nafion and PVDF as binders. Although the modulus of Nafion is smaller than that of PVDF, the curvature and the modulus of silicon/Nafion composite are larger than those of silicon/PVDF electrodes. The moduli of all three composites decrease not only during lithiation but also during delithiation. Based on the measured stress and scanning electron microscopy observations of cracking in the composite electrodes, we conclude that the stress required to crack the composite electrodes with SA and Nafion binders is considerably higher than that of the silicon/PVDF electrode during electrochemical cycling. Thus, the cracking resistance of silicon/SA and silicon/Nafion composite electrodes is higher than that of silicon/PVDF electrodes.

1. Introduction

Lithium ions batteries (LIBs) are the main power source for hybrid electric and electric vehicles because of their high gravimetric and volumetric capacities [1]. Because silicon (Si) can deliver a high theoretical specific capacity of 3579 mAh g⁻¹, it is considered as one of the most promising candidates for the next generation rechargeable LIBs [2]. However, the large volume expansion and contraction (~300%

increase upon full lithiation) of Si can cause significant stresses, leading to pulverization and cracking of Si electrodes [3,4]. The rapid capacity fade and poor cycling performance are major bottlenecks for commercializing Si-based electrodes in LIBs.

Composite electrodes, which are typical in commercial LIBs, have a complex porous structure consisting of active particles, conductive carbon, and polymeric binders. During lithiation/delithiation cycles, the repeated expansion/contraction of active particles may sever the

* Corresponding author. Department of Mechanics, Shanghai University, Shanghai 200444, China.

** Corresponding author.

E-mail addresses: jqzhang2@shu.edu.cn (J. Zhang), yang.t.cheng@uky.edu (Y.-T. Cheng).

contact between particles and the conductive network. Polymeric binders, which are used to keep the particles and conductive carbon physically connected, are therefore critical to the performance and durability of LIBs. It is commonly believed that polymeric binders should be recoverable and chemically stable in the electrolyte and has strong adhesion with the current collector, active particles, and conductive carbon [5,6].

Popular binders for Si electrodes include polyvinylidene fluoride (PVDF), carboxymethyl cellulose (CMC), Nafion, polyacrylic acid (PAA), and sodium alginate (SA) [7–11]. Among them, PVDF is known for its poor accommodation to the large volume change of Si particles [10]. Chen et al. reported that crosslinked elastomeric polymer (PVDF + tetrafluoroethylene + propylene) could be used to maintain a good performance of amorphous Si-Sn electrodes [12]. Li et al. reported that CMC vastly improved cycling performance of Si electrodes with a higher specific capacity and better capacity retention [13]. Garsuch et al. employed lithium-exchanged Nafion as a polymer binder to improve silicon electrode capacity [14]. Mechanical measurements indicate that CMC is a stiffer binder and thus can enhance the mechanical integrity of silicon composite electrodes [8,14]. Magasinski et al. reported the use of PAA, which showed low swelling in carbonate electrolyte and high elastic modulus, as a binder for Si electrodes. The good electrochemical performance was attributed to the high concentration of carboxylic groups in PAA [10]. Similar to CMC and PAA, some polysaccharides extracted from natural products, such as SA, were demonstrated as effective binders for silicon composite electrodes with stable cycling performance [11]. Recently, Xu et al. investigated the role of polymeric binders, including PVDF, SA, Nafion, and Li-ion exchanged Nafion in Si/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC) full cells [15]. By employing partial charge/discharge measurements, they found that the silicon nanoparticles mixed with SA or Nafion binders had better capacity retention compared with that using PVDF. X-ray photoelectron spectroscopy (XPS) measurements showed that the composition of SEI (solid electrolyte interphase) is about the same with different binders [15].

Stress and mechanical properties are believed to play an important role in the performance and durability of electrodes [16]. Intensive efforts have been devoted to understand the effects of stress on the performance and durability of LIBs [17–19]. *In situ* techniques for measuring the changes in strain and stress in battery electrodes have been reported, including digital image correlation (DIC) and curvature measurement method (CMM). Qi and Harris used the DIC technique for real time observation of strain during lithium intercalation in graphite [20]. Jones et al. utilized DIC to measure the strains in a composite graphite electrode and found that an unconstrained composite graphite electrode expands 1.41% during lithiation and contracts 1.33% during delithiation [21]. The MOSS (multi-beam optical sensor system) method has been used to observe the deformation of Si anodes during electrochemical cycling. Sethuraman et al. have conducted a series of experiments using MOSS for *in situ* measurement of stress evolution of a Si-film electrode during lithiation [22–24]. They showed that the elastic modulus of the Si film decreases with the insertion of Li and established the stress-potential relationship for the Li-Si system. Mukhopadhyay et al. used an *in situ* optical approach to analyze stress evolution of the graphite film electrode [25].

The effects of binder on the stress evolution and mechanical property of the Si composite electrode during electrochemical cycling are very important for understanding and predicting the performance and durability of silicon-based electrodes. Sheldon et al. reported the stress evolution of composite electrodes, which is greatly affected by the properties of binders, and the stiffer Na-Alginate binder can induce a larger stress in the electrode than the CMC [26]. However, the effects of binders on the mechanical properties such as elastic modulus and cracking resistance of composite electrodes under electrochemical cycling are still unclear.

We have recently developed an *in situ* stress measurement system by

recording the large curvature change of a bilayer cantilever consisting of a Si/PVDF/carbon black (CB) composite layer on a copper foil [27]. The stress and the elastic modulus of the composite electrode can be obtained from the curvature measurement. In this work, three binders of different physical and chemical properties, Nafion, polyvinylidene fluoride (PVDF), and Sodium Alginate (SA), were selected to investigate the effects of binders on bending deformation, modulus, and stress evolution of composite Si electrodes during electrochemical cycling using the newly developed method [27]. By combining stress measurements with SEM observations of cracks induced by electrochemical cycling, we deduce the effects of binder on the cracking resistance of composite electrodes. In addition, nanoindentation measurements were conducted to obtain the elastic modulus of composite electrodes with various binders.

2. Experimental section

Polyvinylidene fluoride (PVDF), Nafion, and Sodium Alginate (SA) are chosen in this investigation. PVDF is a conventional binder with electrochemical stability at the high voltage range and can be considered as a baseline for developing binders for Si composite electrodes [7]. Nafion has been demonstrated to be a promising binder for nanoparticle silicon electrodes in our previous work [9]. Sodium alginate represents a family of binders with rich carboxylic acid groups, such as CMC and PAA, and its stable cycling behavior in half cells was reported recently [11]. From the mechanical point of view, these three binders have different elastic modulus values [15]. Nafion is the softest, SA the stiffest, and PVDF in-between. A comparative study on them will help us understand how the binder influences the mechanical property evolution and the cracking behavior of composite electrodes during electrochemical cycling.

2.1. Composite electrode preparation

Silicon composite electrodes were made by mixing 50 wt% silicon powder (size 30–50 nm, Nanostructured & Amorphous Materials), 25 wt% conductive carbon black (CB, Super C65, TIMCAL), and 25 wt% binder to form a slurry [15]. Binders used in this work were polyvinylidene fluoride (PVDF, Alfa Aesar), Nafion solution (D-520, Alfa Aesar), and sodium alginate (SA, Sigma-Aldrich). The deionized water was used to dissolve SA and the N-Methyl-2-pyrrolidone (NMP, 99.5%, Alfa Aesar) solvent was used to dissolve PVDF. After mixing, the uniform slurry was cast onto a battery grade Cu foil (24 μm thickness) using a doctor blade (Hohsen) with a gap of 127 μm. The composite electrodes were dried at 130 °C for 12 h in a vacuum oven and densified with the pressure of $0.77 \pm 0.03 \text{ mg cm}^{-2}$ by using a calendaring machine (MTI Corporation) [27]. The final thickness of the composite active layer was 12 μm. The prepared three bilayer electrodes had the same Cu current collector and the same amounts of silicon, carbon black, and binder. Each bilayer electrode was assembled in a quartz cell, see Fig. S1 (supporting information) for details, which was used for electrochemical cycling tests.

2.2. Lithiation/delithiation induced bending

The model cells were charged and discharged repeatedly under a constant current at room temperature using Bio-Logic potentiostats (MPG-2 and VMP-3, BioLogic). The current density of 142.1 mA/cm², which corresponded to 1/20 C-rate based on the theoretical capacity of 3600 mAhg⁻¹ for silicon, was chosen to ensure a uniform lithium distribution in the composite electrode. The prescribed lithiation/delithiation time and cut-off potential were 6 h and 0.01 V versus Li/Li⁺ for lithiation plus 2.00 V versus Li/Li⁺ for delithiation, respectively. An open-circuit relaxation period of 4 min was introduced between lithiation and delithiation. Hence, the lithiation/delithiation would end when either the prescribed time or the prescribed cut-off potential was

attained. The large bending deformation of the bilayer electrodes was induced during electrochemical cycling due to lithium diffusion into silicon particles. The curvature of the bilayer electrodes, κ , with three different binders was measured in real time by using the method developed in our previous work [27] to obtain curvature vs. capacity.

2.3. Extraction of composite modulus and stress from the bending curvature data

The modulus and stress of three composite active layers can be extracted from the curvature data using the method which was proposed in our previous work [27] and is summarized here. Although the composite active layers of bilayer electrode are made of active particles, conductive additive, binder, and micro pores, they are assumed to be macroscopically homogeneous and isotropic. The concentration, c , is defined as the total number of moles of lithium atoms per unit volume of composites. Since the electrode is cycled with a very low C-rate, the lithium concentration can be assumed as a constant across the thickness, which is aligned with the z -axis. In terms of the normalized concentration $\bar{c} = c/c_{\max}$, where $c_{\max}$ is the maximum concentration of lithium in composite, the modulus ratio of current collector to active layer has the following relationship with the thickness ratio, the maximum volumetric strain, the normalized concentration, and the curvature,

$$R_E = \frac{\left[(1 + R_h) \frac{\epsilon_{\max}^* \bar{c}}{\chi \eta_1} - (2R_h^2 + 3R_h + 2) \right] + \sqrt{\left[(1 + R_h) \frac{\epsilon_{\max}^* \bar{c}}{\chi \eta_1} - (2R_h^2 + 3R_h + 2) \right]^2 - R_h^2}}{R_h^3} \quad (1)$$

where $R_E = E_c/E_1$, $E_1(\bar{c})$, and E_c are the modulus of the active layer and current collector, respectively. R_h is the thickness ratio of the current collector to the active layer and is obtained by measuring the thicknesses with a micrometer (Mitutoyo). $\epsilon_{\max}^*$ is the maximum volumetric strain of composite at the fully lithiated state and estimated by the equation $\epsilon_{\max}^* = f\Omega c_{\max}$, where f and Ω are the volume fraction and the partial molar volume of active material. The in-plane strain ϵ_0 and the stress of the active layer are evaluated by

$$\epsilon_0 = \frac{\epsilon_{\max}^* \bar{c} (1 + 3R_H R_H^2 + 4R_H R_H^3)}{3(1 + 4R_H R_H + 6R_H R_H^2 + 4R_H R_H^3 + R_E^2 R_H^4)} \quad (2)$$

$$\sigma_1 = E_1(\bar{c})(\epsilon_0 + \chi\kappa) - \frac{1}{3}E_1(\bar{c})\epsilon_{\max}^* \bar{c} \quad (3)$$

For any given normalized concentration (equal to normalized capacity) the modulus, stress, and strain of composite active layer are calculated by inserting the measured curvature κ , in the above equations.

2.4. Nanoindentation

Nanoindentation measurements were carried out with a diamond Berkovich indenter (tip radius about 200 nm) using a Nano-indenter G200 (Keysight). A depth-controlled mode was used. Before nanoindentation tests, the thermal drift was calibrated to be less than 0.5 nm s^{-1} . The maximum depth and the indentation strain rate were 1500 nm and 0.05 s^{-1} , respectively. The indenter was held for 10 s at the maximum load. Since the maximum indentation depth was less than 1/10 of electrode thickness, the substrate effect could be neglected. The elastic modulus (E) and hardness (H) were determined using the Oliver-Pharr's method [28]. At least 100 nanoindentation tests were conducted on each sample. The indentation results were analyzed with the Gaussian function,

$$f(x) = f_0 + Ae^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (4)$$

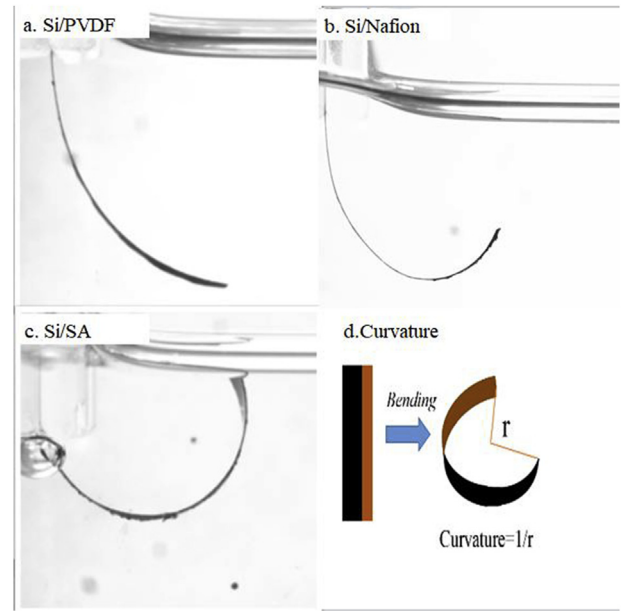


Fig. 1. Photographs of bending of Si composite electrodes with different binders when the normalized capacity is 30%: (a) PVDF; (b) Nafion; (c) SA; (d) a schematic of the electrode curvature.

where μ is the expectation value for either E or H and σ is the standard deviation.

2.5. Other characterizations

After cycling, cells were held for 2 h and then opened inside the glovebox. Silicon composite electrodes were rinsed thoroughly with dimethyl carbonate (DMC, BASF) solvent and dried. The mass and thickness of composite electrodes were measured by a balance (XS205 Dual Range Analytical Balance) and a micrometer (Mitutoyo), respectively. The surface microstructure was characterized by a scanning electron microscopy (SEM, Quanta 250).

3. Results and discussion

Three types of Si composite electrodes are cycled at $C/20$. During lithiation, lithium atoms diffuse into Si particles, causing the active layer to expand. This expansion is restricted by the copper current collector and results in the pure bending of the bilayer electrode. Fig. 1a–c are the captured images of the bent composite electrodes when the normalized capacity is 30%. It is interesting that the lithiation induced curvatures of the three composite electrodes are quite different although they have almost the same composition ratio (see Table S1). This suggests that the binder plays an important role in the lithiation induced deformation of composite electrodes. More specifically, the lithiation induced curvature of the composite electrode is the largest associated with SA binder, the second largest with Nafion binder, and the smallest with PVDF binder. However, it is known that, among the three binder materials, SA has the largest modulus, PVDF the second, and Nafion the smallest [15]. The largest curvature associated with the Si/SA electrode is easily understood because the stiffest binder (SA) makes the composite active layer the stiffest and the volumetric expansion of the stiffest active layer brings the bilayer to undergo the largest bending. However, comparing with PVDF, Nafion has a smaller stiffness but leads to a larger curvature of its composite electrode. This implies that the bending deformation may also be influenced by other factors, which will be given and discussed later.

Fig. 2a and b are plots of the voltage and the curvature vs. time in the first three cycles for the three electrodes. Fig. 2a indicates that the

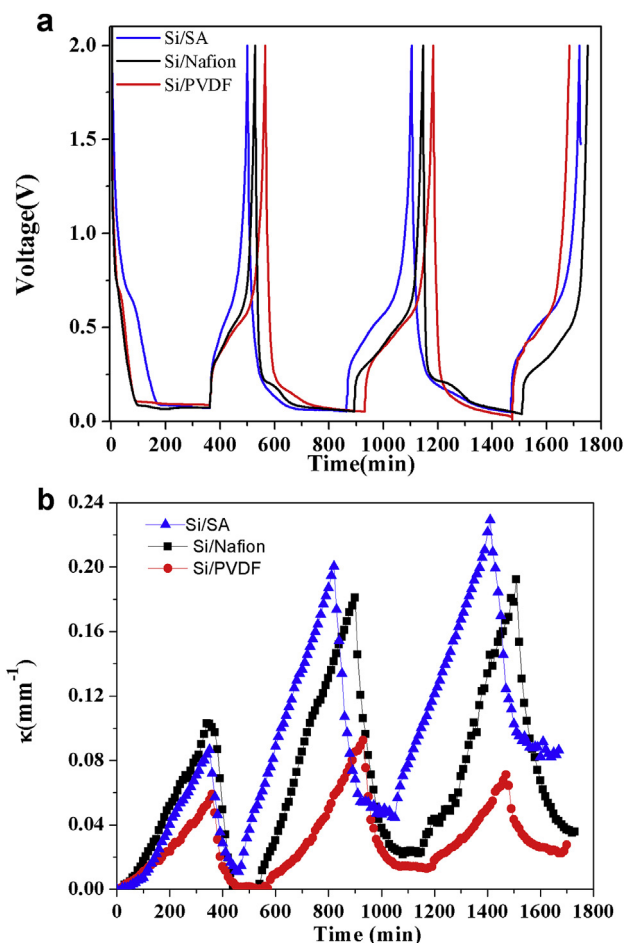


Fig. 2. Voltage (a) and curvature (b) evolution of composite Si/CB/binder electrodes in the first 3 cycles.

lithiation process in each cycle is cut off by the prescribed time (6 h) while the delithiation is cut off by the prescribed voltage (2 V). Therefore, the same amount of lithium reacts with the Si in each cycle. However, some lithium remains in the active material after delithiation. Fig. 2b shows that the curvature change in the first cycle, comparing to the following cycles, is relatively small due to the formation of SEI which consumes a considerable amount of lithium [29]. Therefore, we focus on analyzing data after the first cycle, which can provide more credible information of the effects of binders on the composite Si electrodes. The curvature change in the third cycle is comparable with that in the second cycle for both Si/SA and Si/Nafion composites because of the same lithiation capacity. For the silicon composite electrode with PVDF binder, however, the curvature change in the third cycle is considerably smaller than the change in the second cycle, and this can be attributed to the formation of cracks [27].

The electrode curvature is plotted in Fig. 3 as a function of the normalized capacity during the 2nd cycle. The curvature increases as the lithium content in the electrodes increases and the delithiation process reverses the change in curvature for all three composite electrodes. Among the three composite electrodes the curvature of the composite with sodium alginate as the binder is the largest over the whole capacity range, Nafion the second largest, and the PVDF the smallest.

Due to the large volume change of Si particles upon lithiation, the deformation along the thickness direction in the composite layer is significant (Fig. 4a), which also causes a change in porosity (Fig. 4b). Here, the thickness of the composite electrode is measured with a micrometer (Mitutoyo) and the porosity evolution is calculated using Eqs.

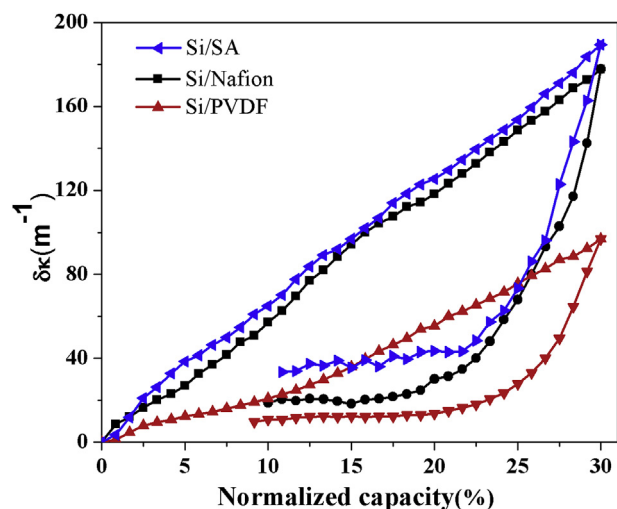


Fig. 3. Curvature change, $\Delta\kappa = \kappa - \kappa_0$, where κ_0 is the initial value of the curvature, of Si/CB/binder composite electrodes in the 2nd cycle.

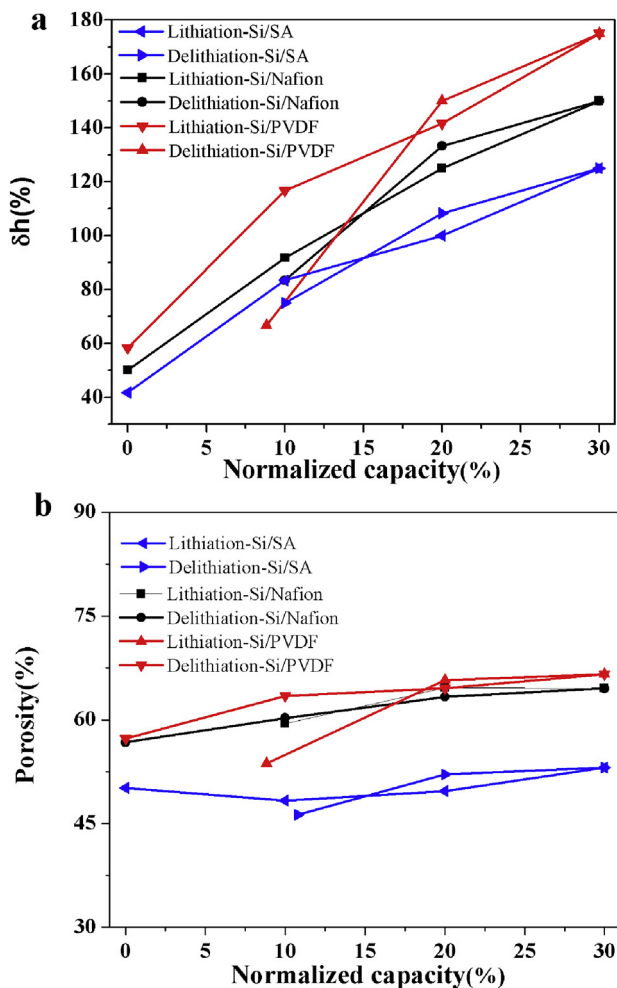


Fig. 4. (a) Relative change in thickness, $\Delta h = (h - h_0)/h_0$, where $h_0 = 12\mu\text{m}$ is the electrode thickness, and (b) porosity evolution of Si composite electrodes with different binders (PVDF, Nafion, and SA) in the 2nd cycle.

S1–S4. Fig. 4a shows an approximately linear thickness increase during lithiation and decrease during delithiation. The Si/SA electrode has the smallest relative change in thickness while the Si/PVDF has the largest relative thickness change. This observation suggests that the SA binder

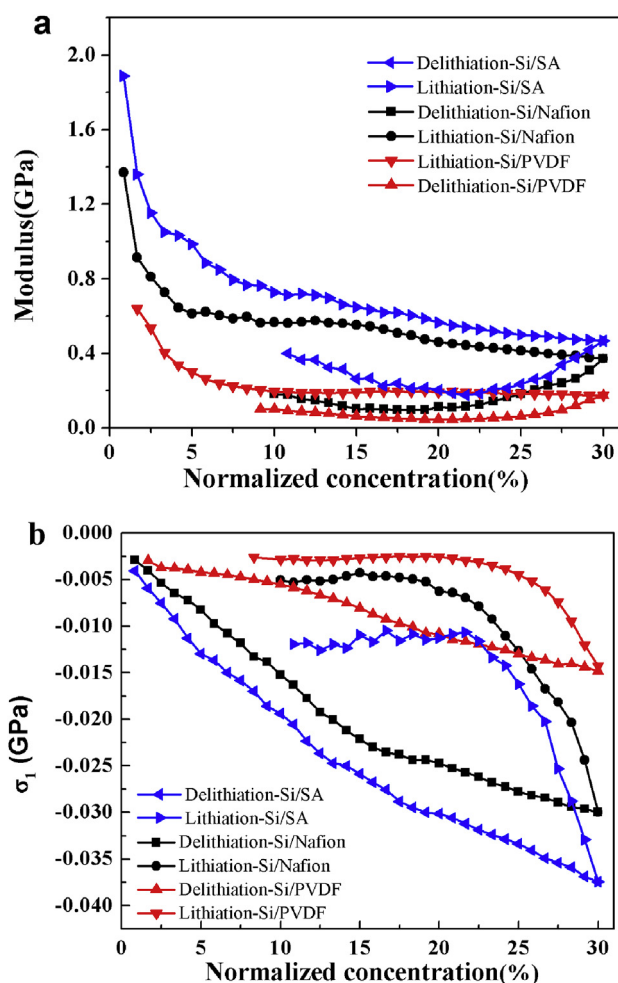


Fig. 5. (a) Elastic modulus and (b) stress evolution of composite electrodes with the normalized lithium concentration in the 2nd cycle.

can provide a stronger restriction on the volume change caused by Si particles, which may help maintain structural stability and thus improve the cycling performance of Si electrodes. Fig. 4b shows that the porosity of the Si composite electrodes changes slightly with lithiation/delithiation despite of a large volume change.

The modulus of Si composite electrodes can be determined by Eq.

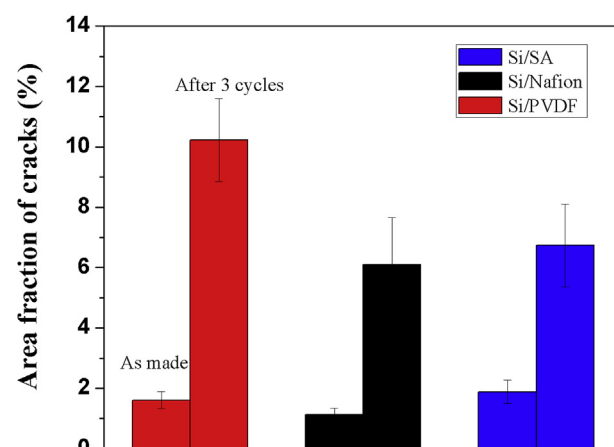


Fig. 7. A comparison of the area fraction of cracks in silicon composite electrodes at the as-made state and after 3 cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(1) with the measured curvature and thickness given in Figs. 3 and 4a. The stress in the composites can be calculated by Eq. (3). Here, the maximum volumetric strain of silicon at the fully lithiated state $\Omega_{C_{max}} = 300\%$ and elastic modulus of current collector $E_c = 117$ GPa [30,31] are assumed and the Si volume fraction in three composites can be found in the supporting materials. Fig. 5a and b are plots of elastic modulus and stress of composite electrodes as a function of the normalized lithium concentration in the second cycle. It is shown that the Si composite electrodes soften significantly during lithiation. The change rate of the composite modulus with Li concentration in the lithiation stage of the electrochemical cycling is very similar for the composite Si electrodes with different binders. The composite elastic modulus, in general, is determined by the elastic modulus and volume fractions of constituents, porosity and cracks. It is known that lithiated silicon softens with increasing Li. Consequently, Si composite electrodes soften with lithiation [32]. The porosity of the electrodes varies slightly during cycling as shown in Fig. 4b and its contribution to the change in composite modulus is negligible. The new cracks formed in the lithiation stage is not severe according to our previous observation [27]. Therefore, the decrease in composite modulus in the lithiation stage is mainly caused by the softening of silicon. The magnitude of compressive stress increases with the lithium concentration during lithiation because more lithium taken by Si can lead to a larger volumetric strain. Therefore, the restriction of current collector results in a higher

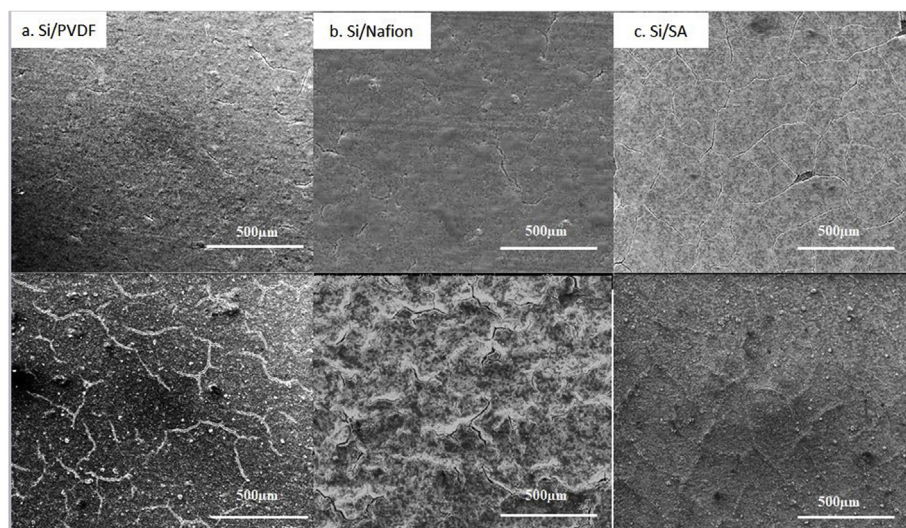


Fig. 6. Surface microstructure of composite electrodes before cycling and after 3 cycles: (a) Si/PVDF, (b) Si/Nafion, (c) Si/SA.

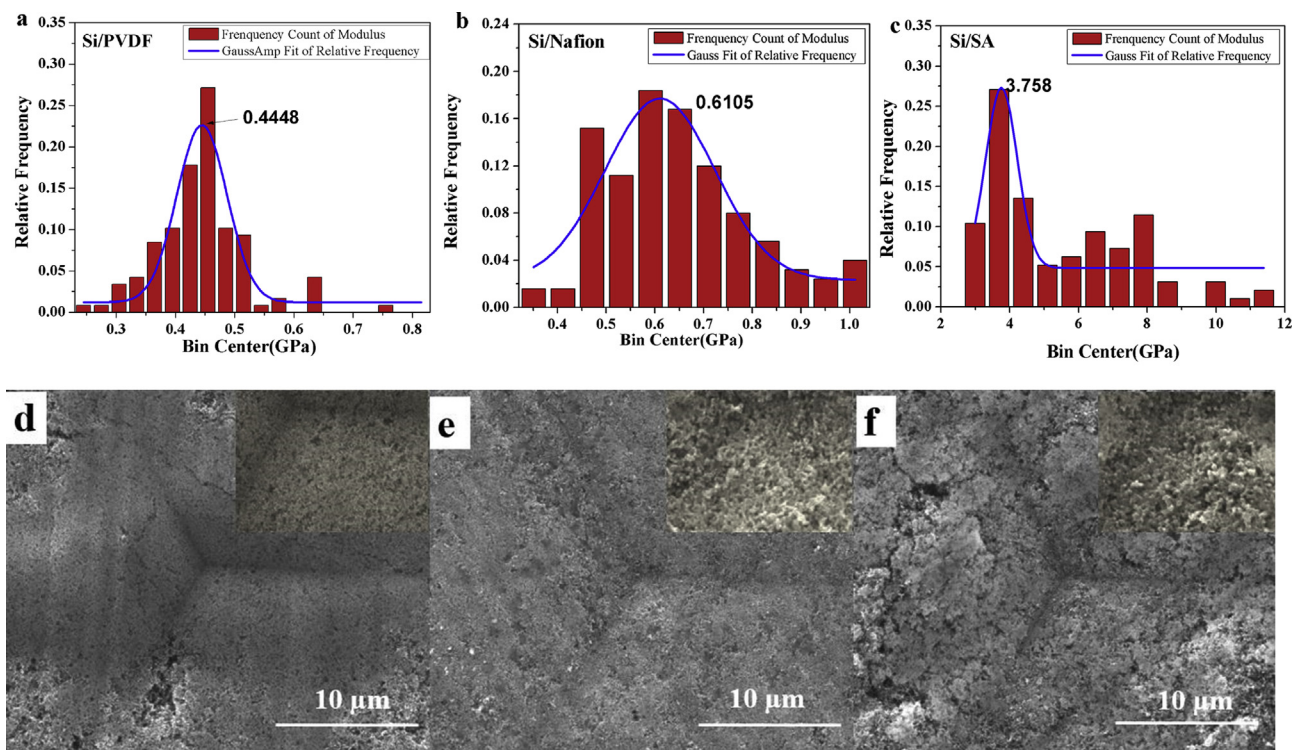


Fig. 8. Statistical distribution of elastic modulus measured by nanoindentation and the microstructure of indents. (a, d) Si/PVDF, (b, e) Si/Nafion, and (c, f) Si/SA.

compressive stress in the composite electrode.

Interestingly, both the modulus and the stress in the delithiation stage recover along a different path from that in the lithiation stage for all three composite electrodes. The modulus and the compressive stress in the delithiation stage are becoming even smaller as delithiation starts. This additional drop in modulus and compressive stress in the composite electrode is believed to be caused by the opening of cracks during delithiation [27]. These cracks are expected to be partially tensile around the pores that exist in the porous composite electrodes, although the overall stress of the electrode layer remains compressive during delithiation.

More importantly, Fig. 5a and b shows that the elastic modulus and the stress differ significantly for different binders. The modulus and compressive stress of composite electrodes with SA as a binder are the highest, the modulus and compressive stress of Si/Nafion are slightly lower, and those of Si/PVDF are the lowest over the range of lithium concentration examined. Since the elastic modulus of Nafion is the smallest among the three binder materials, and the modulus of SA is the largest, that of PVDF is in-between [15] and the composition ratios of the three composites are almost the same, the fact that the modulus and compressive stress of composite with Nafion binder are higher than those of composite with PVDF cannot be explained solely by the modulus and the behavior of constituents in composite electrodes. In order to find the reason the surface morphology of the three types of electrodes before and after electrochemical cycling was examined by scanning electron microscopy (SEM). The SEM images in Fig. 6 show that (1) Si/Nafion and Si/SA composite electrodes have more cracks than that of the Si/PVDF composite electrode before cycling; (2) there is a significant increase in the number of cracks per unit area in the Si/PVDF electrode after three electrochemical cycles; and (3) the crack density and crack pattern in the Si/Nafion and Si/SA composite electrodes do not change much (though the surface roughness changes substantially) after cycling. More specifically, Fig. 7 shows quantitatively the area fraction of cracks, which is the total area of cracks divided by the area of sample, in the three composites before cycling and after three electrochemical cycles. The area fraction of cracks in the Si/

PVDF composite electrode increases by about 5 times after the cycling, while the increments in Si/Nafion and Si/SA composite electrodes are much smaller. This explains well why the modulus of Si/Nafion is higher than Si/PVDF electrodes though PVDF is stiffer than Nafion. Furthermore, these observations, along with the measured stress values reported in Fig. 5b, suggest that Si/Nafion and Si/SA composite electrodes can endure much higher stress without growing or forming as many new cracks as in the Si/PVDF composite electrode. Therefore, we can conclude that the stress to cracking of Si/Nafion and Si/SA composite is higher than that of the Si/PVDF composite. Therefore, Si/Nafion and Si/SA electrodes have a better cracking resistance than Si/PVDF electrodes.

Additional evidence for higher resistance to cracking of Si/Nafion and Si/SA composite electrodes compared to that of Si/PVDF composite electrodes can be found from the curvature evolution curve shown in Fig. 2b. Evidently, the curvature of Si/PVDF in the third cycle is, unlike Si/Nafion and Si/SA, smaller than that in the second cycle, suggesting that more cracks form during the 3rd cycle. Thus, we believe that high crack resistance of Si/Nafion and Si/SA electrodes is one of the reasons why they ensure better electrochemical cycling performance than Si/PVDF electrodes.

Nanoindentation tests were conducted to measure the modulus and hardness of as-made composite electrodes under dry conditions [33]. Because of the random distribution of particles and small voids in the electrodes, the measured values of elastic modulus (E) vary with indentation locations. Fig. 8 shows the modulus histograms of composite electrodes with different binders. Since the indentation depth is much larger than the size of Si particles, the modulus values obtained by indentation represent the volume averaged modulus of the composite electrodes. The increasing trend in the expectation values of E , Si/SA > Si/Nafion > Si/PVDF, agrees qualitatively with that determined from the curvature measurement.

4. Conclusions

An *in situ* curvature measurement method has been developed and

used to determine the effects of binders on bending deformation, elastic modulus, and stress in Si composite electrodes with sodium alginate, Nafion, and polyvinylidene fluoride as binders. The modulus values for Si/SA and Si/Nafion composite electrodes are larger than that of the Si/PVDF composite electrode. All three composite electrodes exhibit substantial reduction in elastic modulus during lithiation. Si/SA and Si/Nafion composite electrodes can bear considerably higher stress than the Si/PVDF composite electrode. The combined analysis of the measured stress and observation of cracking in the three composite electrodes leads to the conclusion that the stress to cracking of Si/Nafion and Si/SA composite is higher than that of the Si/PVDF composite. These results can help explain the good electrochemical performance Si/SA and Si/Nafion composite electrodes and should be helpful to electro-mechanical modeling and developing stable and durable Si composite electrodes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2018.03.048>.

References

- [1] M. Armand, J.M. Tarascon, Building better batteries, *Nature* 451 (2008) 652–657.
- [2] M.N. Obrovac, L. Christensen, Structural changes in silicon anodes during lithium insertion/extraction, *Electrochem. Solid State Lett.* 7 (2004) A93–A96.
- [3] W.J. Zhang, A review of the electrochemical performance of alloy anodes for lithium-ion batteries, *J. Power Sources* 196 (2011) 13–24.
- [4] X.H. Liu, L. Zhong, S. Huang, S.H. Mao, T. Zhu, J.Y. Huang, Size-dependent fracture of silicon nanoparticles during lithiation, *ACS Nano* 6 (2012) 1522–1531.
- [5] D. Mazouzi, Z. Karkar, C.R. Hernandez, P.J. Manero, D. Guyomard, L. Roué, B. Lestriez, Critical roles of binders and formulation at multiscales of silicon-based composite electrodes, *J. Power Sources* 280 (2015) 533–549.
- [6] J. Chen, J. Liu, Y. Qi, T. Sun, X. Li, Unveiling the roles of binder in the mechanical integrity of electrodes for lithium-ion batteries, *J. Electrochem. Soc.* 160 (2013) A1502–A1509.
- [7] Y. Xu, G. Yin, Y. Ma, P. Zuo, X. Cheng, Simple annealing process for performance improvement of silicon anode based on polyvinylidene fluoride binder, *J. Power Sources* 195 (2010) 2069–2073.
- [8] D. Mazouzi, B. Lestriez, L. Roué, D. Guyomard, Silicon composite electrode with high capacity and long cycle life, *Electrochem. Solid State Lett.* 12 (2009) A215–A218.
- [9] J. Xu, Q. Zhang, Y.T. Cheng, High capacity silicon electrodes with nafion as binders for lithium-ion batteries, *J. Electrochem. Soc.* 163 (2016) A401–A405.
- [10] A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C.F. Huebner, T.F. Fuller, I. Luzinov, G. Yushin, Toward efficient binders for Li-ion battery Si-based anodes: polyacrylic acid, *ACS Appl. Mater. Interfaces* 2 (2010) 3004–3010.
- [11] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, A major constituent of brown algae for use in high-capacity Li-ion batteries, *Science* 334 (2011) 75–79.
- [12] Z. Chen, L. Christensen, J.R. Dahn, Large-volume-change electrodes for Li-ion batteries of amorphous alloy particles held by elastomeric tethers, *Electrochem. Commun.* 5 (2003) 919–923.
- [13] J. Li, R.B. Lewis, J.R. Dahn, Sodium carboxymethyl cellulose a potential binder for Si negative electrodes for Li-ion batteries, *Electrochem. Solid State Lett.* 10 (2) (2007) A17–A20.
- [14] R.R. Garsuch, D.B. Le, A. Garsuch, J. Li, S. Wang, A. Farooq, J.R. Dahn, Studies of lithium-exchanged nafion as an electrode binder for alloy negatives in lithium-ion batteries, *J. Electrochem. Soc.* 155 (2008) A721–A724.
- [15] J. Xu, L. Zhang, Y. Wang, T. Chen, M. Al-Shroofy, Y.T. Cheng, Unveiling the critical role of polymeric binders for silicon negative electrodes in Lithium-ion full cells, *ACS Appl. Mater. Interfaces* 9 (2017) 3562–3569.
- [16] D.M. Piper, T.A. Yersak, S.H. Lee, Effect of compressive stress on electrochemical performance of silicon anodes, *J. Electrochem. Soc.* 160 (2013) A77–A81.
- [17] J. Christensen, J. Newman, Stress generation and fracture in lithium insertion materials, *J. Solid State Electrochem.* 10 (2006) 293–319.
- [18] Y.T. Cheng, M.W. Verbrugge, Evolution of stress within a spherical insertion electrode particle under potentiostatic and galvanostatic operation, *J. Power Sources* 190 (2009) 453–460.
- [19] J. Zhang, B. Lu, Y. Song, X. Ji, Diffusion induced stress in layered Li-ion battery electrode plates, *J. Power Sources* 209 (2012) 220–227.
- [20] Y. Qi, S.J. Harris, In situ observation of strains during lithiation of a graphite electrode, *J. Electrochem. Soc.* 157 (2010) A741–A747.
- [21] E.M.C. Jones, M.N. Silberstein, S.R. White, N.R. Sottos, In situ measurements of strains in composite battery electrodes during electrochemical cycling, *Exp. Mech.* 54 (2014) 971–985.
- [22] V.A. Sethuraman, V. Srinivasan, A.F. Bower, P.R. Guduru, In situ measurements of stress-potential coupling in lithiated silicon, *J. Electrochem. Soc.* 157 (2010) A1253–A1261.
- [23] V.A. Sethuraman, M.J. Chon, M. Shimshak, V. Srinivasan, P.R. Guduru, In situ measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation, *J. Power Sources* 195 (2010) 5062–5066.
- [24] V.A. Sethuraman, M.J. Chon, M. Shimshak, V. Srinivasan, P.R. Guduru, In situ measurement of biaxial modulus of Si anode for Li-ion batteries, *Electrochem. Commun.* 12 (2010) 1614–1617.
- [25] A. Mukhopadhyay, A. Tokranov, K. Sena, X. Xiao, B.W. Sheldon, Thin film graphite electrodes with low stress generation during Li-intercalation, *Carbon* 49 (2011) 2742–2749.
- [26] R. Kumar, J.H. Woo, X. Xiao, B.W. Sheldon, 2017. Internal microstructural changes and stress evolution in silicon nanoparticle based composite electrodes, *J. Electrochem. Soc.* 164 (2017) A3750–A3765.
- [27] D. Li, Y. Wang, J. Hu, B. Lu, Y.T. Cheng, J. Zhang, In situ measurement of mechanical property and stress evolution in a composite silicon electrode, *J. Power Sources* 366 (2017) 80–85.
- [28] E.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* 7 (1992) 1564–1583.
- [29] X. Liu, D. Chao, Q. Zhang, H. Liu, H. Hu, J. Zhao, Y. Li, Y. Huang, J. Lin, Z.X. Shen, The roles of lithium-philic giant nitrogen-doped graphene in protecting micron-sized silicon anode from fading, *Sci Rep-UK* 5 (2015).
- [30] Y. Song, X. Shao, Z. Guo, J. Zhang, Role of material properties and mechanical constraint on stress-assisted diffusion in plate electrodes of lithium ion batteries, *J. Phys. D Appl. Phys.* 10 (2013) 105307.
- [31] D.R. Frear, S.N. Burchett, H.S. Morgan, J.H. Lau (Eds.), *The Mechanics of Solder Alloy Interconnects*, Van Nostrand Reinhold, New York, 1994.
- [32] B. Hertzberg, J. Benson, G. Yushin, *Ex-situ* depth-sensing indentation measurements of electrochemically produced Si–Li alloy films, *Electrochem. Commun.* 13 (2011) 818–821.
- [33] Y. Wang, Q. Zhang, D. Li, J. Hu, J. Xu, D. Dang, X. Xiao, Y.T. Cheng, Mechanical property evolution of silicon composite electrodes studied by environmental nanoindentation, *Adv. Energy Mater.* (2018), <http://dx.doi.org/10.1002/aenm.201702578>.