



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 views, 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

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