



# Effects of adhesion and cohesion on the electrochemical performance and durability of silicon composite electrodes



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## HIGHLIGHTS

- Binder/Si interfacial strength strongly affects electrode performance and durability.
- Hydrogen bonding is likely responsible for the strong sodium alginate-Si interface.
- Si particle may become inactive if the binder/Si interface is weak.

## ARTICLE INFO

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## ABSTRACT

Although the choice of binder is crucial in determining the electrochemical performance and durability of silicon-based electrodes, the underlying mechanisms (e.g., mechanical vs. chemical) are unclear. Here, we report a study of the effects of adhesion vs. cohesion on the electrochemical behavior of silicon nanoparticle/polymeric binder/carbon black (CB) electrodes on copper conductor by multiple techniques. Two types of polymeric binders, polyvinylidene fluoride (PVDF) and sodium alginate (SA), were chosen for this study. The results show that because of a sufficiently strong interface between polymer and the copper current collector, both Si/PVDF/CB and Si/SA/CB composite electrode laminates have sufficient adhesive strength with the Cu conductor to cause cohesive failure within the electrode laminate during peel test. However, the interfacial strength between SA and silicon is significantly higher than that between PVDF and silicon, resulting in stronger cohesion within the Si/SA/CB electrode (e.g., peel strength of 78.3 N/m for Si/SA/CB electrode and 8.7 N/m for Si/PVDF/CB electrode, respectively). With a higher cohesive strength provided by a stronger binder-silicon interface, superior cell performance was ensured for Si/SA/CB electrodes. Hydrogen bonding is likely responsible for the stronger SA-Si interface since neither PVDF nor SA bonds covalently with Si according to chemical analysis.

## 1. Introduction

To meet the ever increasing demand in energy storage, tremendous efforts have been devoted to lithium ion battery (LIB) research [1]. Silicon, known for its high theoretical specific capacity (4200 mA h/g), has been intensively studied. Compared with the most commonly used graphite (372 mA h/g) electrode [2–4] in commercial LIBs, Si has the potential to become a negative electrode material for LIBs. However, volume expansion of Si particles can be larger than 300% upon full lithiation, causing pulverization as well as delamination of the electrode layer from the current collector. As a result, the loss of electrical conducting network [5–8], the continuous growth of solid electrolyte interphase (SEI) [9], poor reversibility, and rapidly faded electrochemical performance would occur, impeding the application of Si

composite electrodes in LIBs.

A tether model proposed by Chen et al. showed that the capacity retention of amorphous alloy anodes with 125% volume change was significantly improved by employing a binder with large extension before breakage and good adhesion strength with active material [10]. Si composite electrodes may also benefit from the same approach. However, several investigations demonstrated that stiff and brittle binders actually functioned better in Si composite electrodes than elastomeric binders with much larger elongation to failure [11–14]. Furthermore, a recent publication showed that, among the three binder materials that have been studied, the stiffest binder (sodium alginate) and the softest binder (nafion) both worked much better in Si composite electrodes than PVDF, whose elastic modulus and hardness are in between that of sodium alginate and nafion [15]. Thus, the mechanical

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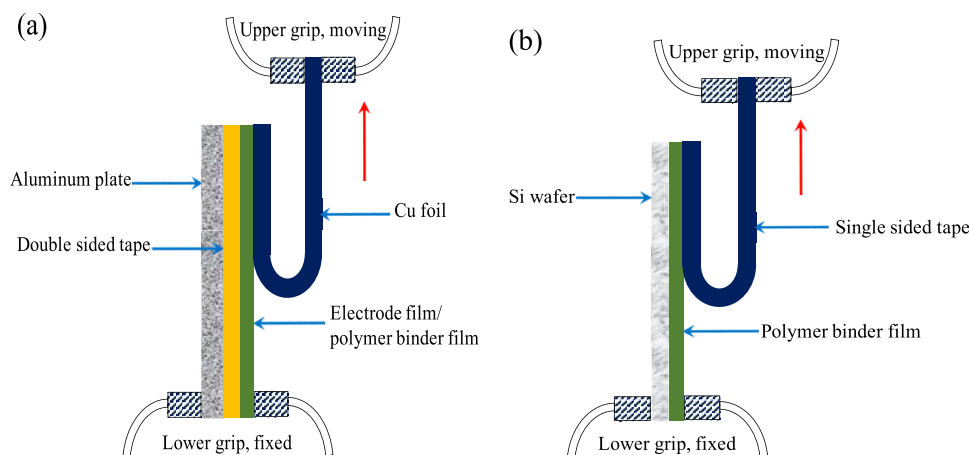


Fig. 1. Geometries employed in peel tests. (a) geometry for the electrode film@Cu foil and polymeric binder film@Cu foil samples; (b) geometry for the polymeric binder film@Si wafer sample.

property of binder material alone does not necessarily correlate with the electrochemical performance of Si composite electrodes. Instead, the interaction between Si and polymeric binder may play a more important role.

The influence of a binder on the adhesion behavior of the electrode laminate on the current collector has also been considered important. Indeed, several studies reported that the employment of an adhesive binder could improve the electrochemical performance of Si composite electrodes by elevating the interfacial strength between electrode and current collector [16–20]. However, Kierzek pointed out, after comparing several binder systems, that the cycling stability was not necessarily enhanced by a higher adhesive strength between the electrode film and the current collector [21].

The adhesion behavior between electrode laminate and current collector may be quantified through a pull-off test according to Haselrider et al. They showed that several failure mechanisms exist in a pull-off test [22]. Depending on where the failure occurs, the measured pull-off stress could be either the adhesive strength between electrode layer and current collector or the cohesive strength within the electrode film. Thus, it is important to carry out detailed microstructure observation to properly interpret adhesion test results.

In the present work, the binder-silicon interfacial strength and its influence on the durability of Si composite electrodes have been studied by carrying out peel tests, electrochemical performance measurements, chemical analysis, and microstructure observation. Our results show that it is not the mechanical property of binder material itself, nor the adhesive strength between electrode film and current collector, but the cohesive strength between the polymeric binder and the Si particles that affects electrode performance the most.

## 2. Experimental section

### 2.1. Electrode preparation and characterization

Silicon powder (size 30 to 50 nm, Nanostructured & Amorphous Materials) was used as the active material, Super C65 carbon black (denoted by CB, TIMCAL) as the conductive agent, PVDF (Alfa Aesar) and sodium alginate (denoted by SA, Sigma-Aldrich) as the binder. PVDF and SA were first dissolved in N-nethyl-2-pyrrolidone (NMP, 99.5% Alfa Aesar) and deionized water (denoted by DI water), respectively. A slurry was then prepared by mixing the Si powder, CB, and binder in a weight ratio of 2:1:1 using a planetary mixer/deaerator (Mazerustar KK-250 S, Kurabo). The Si/PVDF/CB and Si/SA/CB electrodes were made by casting the slurries onto a copper foil. After drying at room temperature for 12 h, the electrodes were transferred into a

vacuum oven to dry for another 12 h at 110 °C. Scanning electron microscopy (SEM, FEI Quanta 250) and optical microscope (Nikon, DXM-1200C) observations were carried out to learn the microstructure of pristine electrodes and electrodes after the peel test.

### 2.2. Polymeric binder film preparation

A homogenous polymer PVDF/NMP (SA/DI) solution was obtained by mixing the solution in the planetary mixer/deaerator for 30 min. The PVDF/NMP (SA/DI) solution was then cast onto a Cu foil/silicon wafer (Wafer World) with a doctor blade. Finally, two types of samples, polymer on copper foil (denoted by polymeric binder film@Cu foil) and polymer on silicon wafer (denoted by polymeric binder film@Si wafer), were dried with the same procedures mentioned in 2.1. Both films have similar smoothness and uniformity by visual inspection.

### 2.3. Peel test

Based on the ASTM D903 standard, several 180° peel tests have been carried out on an Instron 3345 tensile machine with a 10 N load cell. For peel tests of electrode films on Cu current collectors (denoted by electrode film@Cu foil) and polymeric binder film@Cu foil samples, a geometry shown in Fig. 1(a) was employed. Samples of 13 mm in width were pulled at a speed of 50 mm/min. For the polymeric binder film@Si wafer samples, the peel test geometry is shown in Fig. 1(b) without the aluminum plate and double sided tape shown in Fig. 1(a). A 13 mm wide strip of polymer binder film was obtained by using a knife to cut and remove the excess material. A piece of single sided tape (40 PR, 3M Company) was pulled by the upper grip at the same speed to test the adhesive strength between binder and silicon wafer. Photographs of the peel test setup shown in Fig. 1(a) and (b) are shown in Fig. S1(a) and Fig. S1(b), respectively.

### 2.4. Chemical analysis

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS10, Thermo Scientific) and x-ray photoelectron spectroscopy (K-Alpha XPS system, Thermo Scientific) were employed to investigate the possible chemical interactions between binder and Si in powder samples (PVDF + Si powder mixture and SA + Si powder mixture) and cast samples (PVDF + Si cast and SA + Si cast). The powder mixtures were prepared by mixing the Si particles and binder powders in a weight ratio of 2:1 in an alumina mortar. For cast samples, a slurry was first made by mixing the powders of Si and binder with solvents (NMP for PVDF and DI water for SA) in the same 2:1 weight

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