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Low-cost and sustainable corn starch as a high-performance aqueous binder in silicon anodes via *in situ* cross-linking

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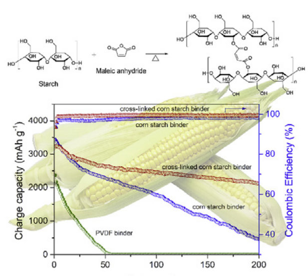
HIGHLIGHTS

- Low-cost corn starch was used as a high-performance binder in silicon anodes.
- Corn starch was *in situ* cross-linked by maleic anhydride.
- The Si anode with the cross-linked corn starch binder improves cell performances.

GRAPHICAL ABSTRACT



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ABSTRACT

In situ cross-linked corn starch is used as a binder in silicon (Si) composite anodes for enhancing the cycling stability of lithium-ion batteries. The corn starch binder is *in situ* cross-linked by maleic anhydride during the fabrication of Si anodes. The cross-linking reaction of corn starch is investigated by infrared spectroscopy, solid-state ^{13}C nuclear magnetic resonance spectroscopy and thermal gravimetric analysis. The results show that the hydroxy groups of corn starch react with maleic anhydride to form ester linkages, which eventually form a three-dimensional network structure. The cross-linked corn starch binder significantly enhances the adhesion of the Si/conductive carbon composite on the copper current collector. Peeling test experiments show that the adhesion force of the cross-linked corn starch binder is 4.9 times higher than that of the corn starch binder without cross-linking. Moreover, the cell performance tests show that the Si composite cathode with the cross-linked corn starch binder exhibits a high specific capacity of 3720 mAh g^{-1} and enhances cycle-life performance. This *in situ* cross-linking approach underscores the potential of corn starch, which is a low-cost and environmentally sustainable material, as a binder for the Si composite electrodes to improve its electrochemical performance.

1. Introduction

Lithium-ion battery technology has been in pursuit of developing high-performance battery materials to deal with the incessant increasing demand of energy. Silicon (Si) is one of the potential candidates as high-energy-density anodes because of its high theoretical specific capacity of 4200 mAh g^{-1}, which is almost tenfold higher than the value of the commercially used graphite (372 mAh g^{-1}) [1–3].

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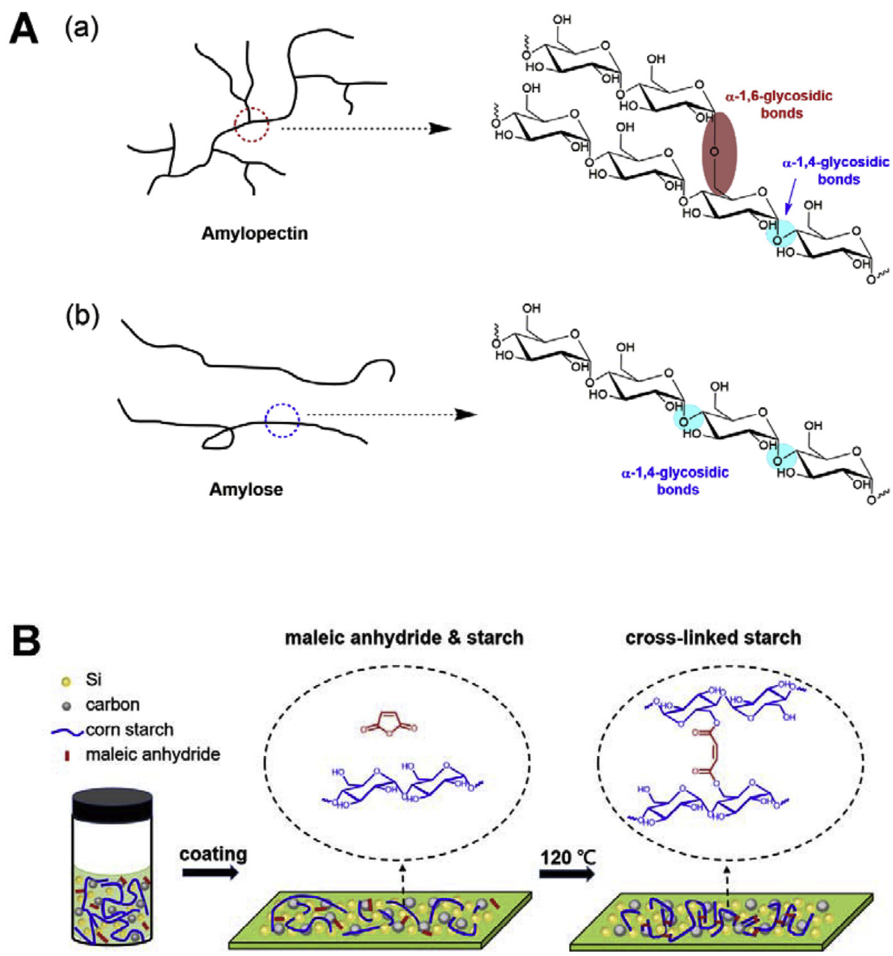

Fig. 1. (A) Schemes and chemical structures of (a) amylopectin and (b) amylose of corn starch. (B) Fabrication process of Si composite electrode with cross-linked corn starch as a binder and maleic anhydride as a cross-linker.

Despite possessing such a high capacity, Si anodes also have the advantages of having a low discharge potential (~0.5 V *vs.* Li/Li^+), high abundance and environmental benignancy. However, the performance of Si anodes is affected by the large volume changes (~300–400%) during the lithiation and delithiation of Si [2,4,5]. The huge-volume change of Si causes detrimental effects, such as the pulverization of Si and the cracking of electrodes, to the cycle-life performance of batteries [6]. Several approaches have been proposed to deal with this cycle-life issue [3], including the use of nano-sized Si to enhance mechanical integrity [7–9], composite electrodes (Mg_2Si, $CaSi_2$, NiSi, FeSi, Si/conducting polymers and Si/graphene) to maintain the electrical conductivity [10–14], Si core-shell structures with void space for volume expansion [15–17] and nanoporous Si to buffer the volume expansion [18].

As the volume of Si changes dramatically, the interactions among the binder, Si-active material, conductive carbon and the Cu current collector become weak, which eventually causes a decrease in the cycling performance as well as battery failure due to loss of electrical contact [6]. In such a scenario, the role of a binder becomes very crucial not only to keep the electrode intact but also to achieve an adequate cycling performance [19]. Therefore, the uses of several binders have been reported, such as sodium carboxymethyl cellulose (CMC) [20], CMC-styrene butadiene rubber (SBR) [21], poly(acrylic acid) (PAA) [22], sodium polyacrylate (NaPAA) [23], NaPAA-*g*-CMC [24], poly (vinyl alcohol) (PVA)/PAA [25], acrylic acid/poly(ethylene oxide) (PEO)-diallyl ether copolymer [26] and conducting polymers [27]. Recently, several natural binders have been also proposed, including chitosan [28,29], sodium alginate [30–32], β-cyclodextrin polymer [33], gum arabic [34], gellan gum [35], xanthan gum [36], guar gum [1,37,38] and karaya gum [39] binders. These binders, being polymers of glucose and abound in hydroxy groups, may interact with Si to enhance the mechanical property of the Si anodes. Indeed, to enhance the cycle-life performance, the binders should have excellent stability and mechanical properties. Finally, the cost and sustainability of binders have to be considered as well.

Starch is one of the cheapest natural carbohydrate binders. The presence of several hydroxy groups in starch can enhance its interaction with the Si particles using the formation of multifaceted hydrogen bonds [1,33]. Unmodified waxy corn starch predominantly contains amylopectin (a branched structure, Fig. 1A–a) and a trace amount of amylose (a linear structure, Fig. 1A–b). The highly branched structure of amylopectin comprises glucose units with both α-1,4- and α-1,6-glycosidic bonds, whereas amylose comprises glucose units with only α-1,4-glycosidic bonds [40]. The 1,4-linked linear structure is responsible for gelling properties [41]; the 1,6-linked branched structure forms weak gels [42]. Since gelation in the slurry is not suitable for electrode casting [43], corn starch may be a good candidate as a binder of cathodes. For example, oxidized starch has been reported as a binder for Si anodes in lithium-ion batteries [44]. Herein, we propose waxy corn starch as an economical, effective and high-performance binder for Si composite anodes. The exclusivity of the effort also involves an *in situ* cross-linking approach to form a three-dimensional (3D) network structure to enhance the mechanical property of Si composite electrodes (Fig. 1B). The mechanical property and structure of the Si composite electrode with the cross-linked corn starch binder are studied by peeling test and scanning electron microscope (SEM), respectively. The