



# Dual-crosslinked network binder of alginate with polyacrylamide for silicon/graphite anodes of lithium ion battery

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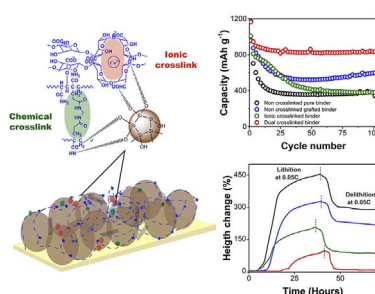
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## HIGHLIGHTS

- A bio-derived alginate is grafted with a strongly adhesive polyacrylamide.
- The dual-crosslinking is achieved by ionic and chemical crosslinkers.
- The dual-crosslinked binder has strong adhesion with low electrolyte uptakes.
- The dual-crosslinked binder helps to prevent extra volume expansion during cycle.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

In lithium ion batteries, high-capacity anodes that undergo very large volume change during charge/discharge cycles are needed to apply a strongly adhesive polymer binder due to the severe mechanical stress developed during the cycles. Although bio-derived alginate is known to be a potential candidate for the binder owing to its strong mechanical property, it can be improved using a number of modifications such as physical crosslinking. Here, we propose a significantly better method of improving the electrochemical performance of the binder by introducing dual-crosslinked alginate with polyacrylamide. The polyacrylamide provides strong adhesion in the electrode with resistance to the penetration of the organic electrolyte. Both ionic and covalent crosslinkings in the binder maintain their intrinsic good binding properties and additionally enhance lithium ion diffusion. More interestingly, an in-situ electrochemical dilatometer study indicates that the dual-crosslinked binder is considerably helpful to prevent volume expansion beyond the inevitable value caused by active materials in electrodes during the cycle. Consequently, the Si/C (1/3) electrode retains nearly 840 mAh g<sup>-1</sup> high capacity even after one hundred cycles with excellent cycleability.

## 1. Introduction

The application of lithium ion battery (LIB) has rapidly increased in various areas such as in portable electronic devices and electric vehicles including hybrid electric vehicles. Graphite has been widely used as an anode material for more than 20 years because of its good capacity retention, high conductivity, and low cost, even though its electrochemical performance is strongly affected by the other components of

the electrode such as conductive materials and binder [1–3]. Until now, polyvinylidene difluoride (PVDF) has been the most common polymer used as a binder due to its good electrochemical stability with some adhesion to electrode materials and current collector [4–7]. However, PVDF requires the use of a toxic and expensive organic solvent, *n*-methyl-2-pyrrolidone, during the manufacturing process of LIBs. Since water is very attractive as an alternate to the organic solvent, eco-friendly water-based binders composed of both water-dispersed

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styrene-butadiene rubber (SBR) and water-soluble carboxymethyl cellulose (CMC) have been successfully employed as a binder system for graphite electrodes [8–12]. However, the water-dispersed SBR was not appropriate for high-capacity active materials such as silicon or tin, which undergo significant volume change during the charge/discharge process due to their spot contact mechanism with active materials. Rather, the sole use of CMC has shown to be superior for high-capacity materials, even though a relatively large amount of CMC is used [11]. Recently, synthetic or bio-derived water-soluble polymers containing carboxyl groups, such as alginate and polyacrylic acid (PAA), demonstrated promising binder characteristics for high-capacity silicon and silicon/graphite anodes, due to the high adhesion of carboxyl groups [13–16]. Kovalenko et al. [17] reported that the Si anode with alginate binder exhibited a stable capacity of 1700 mAh g<sup>-1</sup> up to 100 cycles, which was significantly better than that with PVDF or Na-CMC binder. Liu et al. [18] and Yoon et al. [19] proposed a calcium-crosslinked alginate as a novel binder for a Si/C composite anode. In their results, the crosslinking in alginate improved the mechanical properties of the binder when compared to sodium alginate and other commercial binders, and ultimately increased the capacity of the Si/C anode with a stable cycleability. Other water-soluble binders such as poly(acrylamide-co-diallyldimethylammonium chloride) (PAMAC) have been reported for graphite electrodes [20]. PAMAC binder was shown to assist the formation of a more conductive solid electrolyte interface (SEI) and faster penetration of electrolyte in the graphite anode compared to a typical PVdF binder. Consequently, the graphite anode with PAMAC was able to retain constant dimensions even at an elevated temperature. The polyacrylamide (PAAm) also helped to retain the original networks of the electrode in the course of charge/discharge. Tensile experiments have shown that PAAm fully recovers its original dimension after unloading [21].

In spite of these endeavors, further improvement of the electrochemical performance of electrodes is still required. In particular, high-capacity anodes have not exhibited sufficiently stable cyclic performance for commercial application. Developing new polymer binders may be a critical factor to achieve their commercial application. In this study, dual-crosslinked binder systems are first introduced for a high-capacity silicon/graphite electrode, which can be treated in a water solvent. The dual-crosslinking is achieved by grafting alginate with PAAm, with the physical and chemical crosslinking of alginate grafted with PAAm. The novel characteristics of the dual-crosslinking in the grafted binder are investigated using a variety of characterization techniques.

## 2. Experimental

**Synthesis of alginate-g-polyacrylamide:** Sodium-alginate (Na-Alg) grafted with PAAm was synthesized by grafting PAAm onto Na-Alg using a free radical polymerization method in an aqueous system [21–23]. 2.8 g of Na-Alg (Alfa Aesar Co. Ltd) and 10 g of acrylamide monomer (AAM, Junsei chemical. Co, Ltd) were dissolved in 80 ml distilled water overnight in a 250-ml four-necked flask equipped with a mechanical stirrer, a reflux condenser, a nitrogen line, and a thermometer. The solution was then heated to 50 °C in a water bath and the temperature was maintained during the subsequent polymerization. For the polymerization of AAM, 0.06 g of ammonium persulfate (APS) initiator was first added to the solution, followed by the addition of 0.055 g of tetramethyl-ethylenediamine (TEMED) after 30 min as a reaction accelerator. These chemicals were purchased from Sigma-Aldrich. Here, the weight ratios of APS and TEMED to AAM were 0.006 and 0.0055, respectively, in order to produce an optimized graft copolymer. This grafted polymerization was continued for 3 h to produce a complete alginate grafted with polyacrylamide (Alg-g-PAAm), as shown in Fig. 1.

**Preparation of crosslinked polymers:** Alg can be physically crosslinked by a number of metal ions such as calcium, aluminum, iron,

and zinc ions [24]. Here, CaCl<sub>2</sub> (Daejung Chem. Metals Co. Ltd) was used for the physical crosslinking of alginate chains in the Alg and Alg-g-PAAm samples. For the chemical crosslinking of PAAm chains, N,N'-methylenebis(acrylamide) (MBAA, Sigma Aldrich Co. Ltd) chemical crosslinker with APS was used for the Alg-g-PAAm samples [21,24]. Either non-crosslinked Alg or Alg-g-PAAm was dissolved in distilled water and stirred at room temperature to form 5 wt.% solution. Specific amounts of CaCl<sub>2</sub>, or CaCl<sub>2</sub> and MBAA with APS were then added to the non-crosslinked solutions and stirred for 30 min, leading to high viscosity hydrogels. For the purpose of characterization only, these hydrogels were exposed to a temperature of 80 °C in a convection oven for 4 h to form physical or physical-chemical crosslinking. The formation of the crosslinking is confirmed by the naked eye as shown in the photos. For convenience, physically crosslinked-Alg and dual (physically and chemically) crosslinked-Alg-g-PAAm are hereby noted as *c*-Alg and *c*-Alg-g-PAAm, respectively. Two non-crosslinked and two crosslinked polymer films cast from their solution were used for the following characterization techniques.

**Characterization of polymer binders:** The Fourier Transform-Infrared (FT-IR) spectra of non-crosslinked polymers (Alg and Alg-g-PAAm) and crosslinked polymers (*c*-Alg and *c*-Alg-g-PAAm) were obtained to confirm the existence of functional groups. FT-IR (Thermo Scientific Nicolet iS5 Infrared Spectrometer) was conducted in the range of 4000–400 cm<sup>-1</sup> using potassium bromide pellets. The electrolyte uptake of the binder films was also studied through an electrolyte absorption test. Dry binder film was initially weighed ( $W_{\text{before}}$ ), immersed in the mixed solvents composed of ethylene carbonate (EC): diethylcarbonate (DEC): dimethyl carbonate (DMC): (1:1:1 by volume) at room temperature for 24 h, and weighed ( $W_{\text{after}}$ ) again after the removal of excess electrolyte from their surface. The swelling ratio was calculated as

$$s = \frac{W_{\text{after}} - W_{\text{before}}}{W_{\text{before}}} \times 100\%$$

**Preparation of electrodes:** Since the crosslinked polymers did not dissolve in water, the crosslinking agents were added in the course of slurry preparation. Subsequent drying processes made the polymer binder crosslinked while the electrodes were dried. Initially, the 5 wt.% non-crosslinked binder solutions such as Alg and Alg-g-PAAm were mixed with silicon, graphite, and water-dispersed carbon nanotube as a conducting agent. The contents of silicon and graphite as active materials were 19% and 57% in the solid of the electrode slurry, respectively, whereas those of the binder and conducting agent were 15% and 9%, respectively. For crosslinked electrodes, very small amounts of CaCl<sub>2</sub> or CaCl<sub>2</sub> and MBAA with APS were added to the Alg- or the Alg-g-PAAm-containing slurries, respectively. The resultants were coated onto copper foil, dried in a convection oven at 70 °C for 30 min, and then vacuum dried at 70 °C overnight. The mass loading of electrodes was controlled to be approximately 1.3 ± 0.1 mg cm<sup>-2</sup>.

**Characterization of electrodes:** Using a texture analyzer (TA-PLUS, Lloyd Instruments Ltd.), the adhesion strength of electrodes was obtained by measuring the 180° peel strength of the electrode strips with the peel rate of 50 mm min<sup>-1</sup>. To investigate the interaction between binders and Si nanoparticles, FT-IR spectroscopy was again employed. The morphology of the electrodes was studied by scanning electron microscopy (SEM).

For electrochemical characterization, CR2032-type coin-half cells were assembled in an argon-filled glove-box using the Si/C working electrode, Li foils as a counter and reference electrodes, 1.15 M LiPF<sub>6</sub> in EC:DEC:DMC (3:5:2 v/v%) with additive as 5wt.% FEC (fluoroethylene carbonate), 2wt.% VC (vinylene carbonate), and 0.4wt.% LiBF<sub>4</sub> as an electrolyte, and polypropylene film as a separator. Galvanostatic charge/discharge was performed between 0.005 and 2 V. Electrochemical impedance spectroscopy (EIS) with a frequency range of 100 kHz to 0.01 Hz and cyclic voltammograms (CV) of the coin-half

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