



## Short Communication

# Improvement of the characteristics of poly(acrylonitrile–butylacrylate) water-dispersed binder for lithium-ion batteries by the addition of acrylic acid and polystyrene seed



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## ABSTRACT

In this study, we modified an attractive water-dispersed poly(acrylonitrile–butylacrylate) binder used for lithium-ion batteries by the addition of highly acidic acrylic acid (AA). The synthesized poly(acrylic acid–acrylonitrile–butylacrylate)–polystyrene polymer showed an improved performance as a binder with smaller particle size, stiffer polymer matrix, higher adhesion strength, and lower contact angle characteristics. Consequently, the modified water-dispersed binder by the addition of AA increased the cyclic capacity and retention of physically mixed silicon/graphite anodes, when compared to the unmodified poly(acrylonitrile–butylacrylate) binder.

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## 1. Introduction

In recent years, polymer binder, an inactive component of lithium-ion battery (LIB) electrodes, has received considerable attention, because the electrochemical behavior of electrodes can be improved to a certain extent by using an appropriate polymer as a binder [1–5]. While a conventional polyvinylidene fluoride (PVdF) binder has been receiving less and less attention, some interesting and promising polymeric binders have been claimed for the negative electrodes of LIBs [5–9]. Although less attention has been given to the cathodic polymer binder, there have been many reports that specific polymers could improve the electrochemical stability of the cathodes [10–13]. In the perspective of commercial LIB manufacturing process, water-based binders such as water-soluble carboxy methyl cellulose (CMC) [14–16], water-dispersed styrene–butadiene rubber (SBR) [17,18], and more recently poly(acrylonitrile–butylacrylate) (P(AN–BA)) [19] have been receiving significant attention from industry because they could facilitate environmental-friendly manufacturing process of LIBs. In particular, the water-dispersed binders connect active materials by point-to-point so that the content of binder in electrodes can be reduced when compared to typical water- or organic-soluble binders [20]. However, these water-dispersed

binders have not been studied in detail. Therefore, in this study, we successfully developed a new water-based binder with an improved anodic performance of LIBs.

In our previous study [19], we demonstrated that the water-dispersed P(AN–BA) binder synthesized by the seedless emulsion polymerization was very effective to graphite electrode as a binder, compared to the commercial SBR binder. The seedless emulsion polymerization was switched to a seeded emulsion polymerization in order to synthesize more uniform particle sizes of the binder. We investigated and optimized the amount of polystyrene (PS) seed used in the emulsion polymerization and synthesized a water-dispersed P(AN–BA)–PS. To further improve the electrochemical performance of the P(AN–BA)–PS binder, highly polar acrylic acid (AA) was added and finally we synthesized a superior water-dispersed P(AA–AN–BA)–PS binder, which was copolymerized with AA monomer during the seed emulsion polymerization of the P(AN–BA)–PS.

## 2. Experimental

Three monomers, acrylic acid, acrylonitrile, and butylacrylate, were purchased from Junsei Chemical Co., Ltd., Japan. Water-dispersed PS seeds with 37 nm average diameter were provided by Hansol Chemical Co. in Korea. Commercial grades of potassium persulfate (KPS, Sigma–Aldrich) and sodium dodecyl sulfate (SDS, Tokyo Chemical Industry Co.) were also used as the initiator and emulsifier, respectively, for the polymerization.

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**Table 1**  
Amounts of monomers used for the emulsion polymerization.

	PAB	PABS	PAABS
PS seed (g)	0	3	3
AN/BA (g/g)	10/20	10/20	10/20
AA (g)	0	0	1

To synthesize the binder, PS seeds were initially mixed with the SDS emulsifier and an aqueous mixture of the monomers in a four-necked flask equipped with a reflux condenser under nitrogen bubbling at 70 °C for 1 h. Herein, the ratio of AN to BA was 0.5 in the aqueous mixture, exhibiting the best binder performance for graphite electrodes [19]. The optimum amount of PS seed was chosen from the results of preliminary tests (shown in Table S1 and Fig. S1 of the Supplementary data). Exact amounts of the monomers are listed in Table 1. Then, a small amount of KPS (approximately one part of the total amount of monomers) dissolved in water was added to the reactor under a nitrogen atmosphere. The polymerization was performed for 4 h for the completion and stabilized for 24 h before tests. For simplicity, P(AN–BA), P(AN–BA)–PS, and P(AA–AN–BA)–PS are abbreviated as PAB, PABS, and PAABS, respectively.

Similar to our previous study [19], the particle size distribution was measured using a Microtrac S3000 apparatus. The contact angle of the binder film was measured by an optical tensiometer (Theta Lite, Biolin Scientific) after 1 min exposing to an electrolyte droplet. The gel content was calculated by immersing a polymer film in tetrahydrofuran and stirring at room temperature for 6 h, and then the weight percentage of the undissolved polymer to the total weight of the polymer films was measured and denoted as the gel content. The polymer films coated on Cu foil were also fully soaked in the electrolyte solution (1:1:1 EC:DMC:EMC by volume) for 24 h. The change in weight before and after the soaking was used to calculate the electrolyte uptake of the binder.

The water-dispersed polymers (9 wt.%) were mixed with 60 wt.% nanosized silicon (KCC Co., diameter = 20–30 nm), 20 wt.% graphite (GX15C, Carbonix Co., diameter = 10–12 μm), 5 wt.% vapor grown carbon fiber, and 6 wt.% high viscous CMC (Daicel FineChem Ltd.) in a planetary ball mill (Pulverisette 7, Fritsch) for 1 h. The resulting slurry was then coated on a Cu-foil and dried in a convection oven at 60 °C for 30 min and subsequently in a vacuum oven at 80 °C for a day before further tests. The electrode loading was  $3.0 \pm 0.1 \text{ mg cm}^{-2}$ . A texture analyzer (TA-Plus, Lloyd Instruments Ltd.) was used to determine the adhesion strength of the electrodes before and after 24 h soaking in the electrolyte solution by measuring the 180° peel strength of the electrode strips. Other electrochemical tests were performed following the same procedures as described in our previous study [19].

### 3. Results and discussion

The effect of AA including PS to the water-dispersed PAB binder was first investigated by studying some physical properties. As shown in Table 2, the average particle sizes became smaller for the PABS and PAABS samples synthesized using PS seeds when compared to the PAB. In particular, large-sized PAB particles disappeared in the PS seeded polymerization; therefore, PABS and PAABS had more uniform particle size distribution (see Fig. S2 in the Supplementary data). This is one of the advantages of the emulsion polymerization with nanosized seeds. High-capacity active materials such as Si accompany dramatic volume changes during their charge/discharge processes. The smaller the binder particles are, the better the high-capacity electrode structures maintain during cycles, because smaller binder particles can more

**Table 2**  
Physical properties of the water-dispersed binders.

	PAB	PABS	PAABS
Average particle size (nm)	146 <sup>a</sup>	100	84
Gel content (%)	0 <sup>a</sup>	69.8	78.8
Electrolyte uptake (%)	107.1	52.9	50.0
Contact angle (°)	50.7 ± 4.3	62.7 ± 2.9	49.2 ± 3.2
pH	3.38	1.94	1.82

<sup>a</sup> These data were reproduced from our previous work [19].

effectively release stresses generated during the charge/discharge process.

In the perspective of lithium ion transport through the binder film, it is favorable for polymer binder to absorb electrolyte. In contrast, the absorption is detrimental to the adhesion capability of the binder, because the swelling of the binder consequently weakens its adhesion to active materials or current collector. In particular, the high-capacity anodes require highly adhesive binders to tolerate significant volume change; therefore, the electrolyte uptake of the binder must be controlled very carefully in comparison to binders used for other anodes such as graphite and lithium transition-metal oxide. The water-dispersed binder can control the amount of electrolyte uptake normally through the type and ratio of monomers, and the gel content indicates the extent of crosslinking. The increase in the gel content by the formation of crosslinking network disturbs the mobility of polymer chains, thus polymer chain can limit electrolyte permeation and maintain its rigidity even after electrolyte uptake. Highly stiff polymers such as Na-CMC, alginate, polyacrylic acid, and polyvinyl alcohol have been claimed to be superior in the binder performance of the high-capacity electrodes compared to that of the flexible polymers [1,15,21–23]. As listed in Table 2, the PABS and PAABS samples, exhibiting high gel content and thus low electrolyte uptake might be more favorable for the high-capacity anodes as the binders than the PAB, absorbing larger amount of the electrolyte. Furthermore, the addition of AA again decreases the electrolyte contact angle increased by the addition of PS seeds. It is attributed to the affinity between carboxyl acid and carbonate, because both of them contain C=O carbonyl groups. A relatively small contact angle indicates more rapid permeation of the electrolyte.

Although the effect of pH of the water-dispersed binders is ambiguous at present, the PS seed solution provided by industry has a much lower pH value than that of the PAB sample, lowering the pH of the PABS sample. Moreover, the addition of AA to the water-dispersed binder increases the acidity by the dissociation of carboxyl groups, and thus slightly decreases pH value as shown in Table 2. The carboxyl groups including their dissociated anionic sites in AA are expected to increase the adhesion capability of the binder due to the formation of covalent bonds with the polar functional groups on the surface of active materials [21]. However, the results shown in Fig. 1 revealed that the adhesion strength of the fresh electrode, measured by the 180° peel tests, did not improve significantly by adding AA. Nevertheless, the drop in the adhesion strength after soaking electrodes in the electrolyte solution was the lowest when the PAABS binder was used, and it showed the highest adhesion of the binders under the circumstance similar to real electrode situation. PAABS binder retained 63.6% of the adhesion strength, whereas the PAB and PABS samples retained only 50.5% and 51.2% of the adhesion strength, respectively, after soaking in the electrolyte. As mentioned above, this phenomenon occurs, because of a relatively high gel content and low electrolyte uptake of the water-dispersed PAABS binder. Moreover, the adhesion formed by the anionic sites in AA may be less susceptible to the electrolyte soaking than that by physical bonds such as the van der Waals interaction. Besides, the PAABS was revealed to be

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