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Short communication

Application of a new acrylonitrile/butylacrylate water-based binder for negative electrodes of lithium-ion batteries

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ABSTRACT

This communication introduces a new, environmentally friendly, water-based binder, poly(acrylonitrile-butylacrylate) (P(AN-BA)), for negative electrodes of lithium-ion batteries. Butylacrylate (BA) and acrylonitrile (AN) with three different weight ratios were chosen as monomers to synthesize a series of emulsion copolymers. These products were then used as potential binders for graphite anodes, and their electrochemical performance was compared to the conventional styrene-butadien rubber (SBR) binder. The binder synthesized with a 1/2 weight ratio of AN/BA was the optimal combination for graphite electrodes due to its flexibility with good adhesion, resulting in a high diffusion coefficient and capacity for lithium ions. These contributed to the electrochemical performance of the P(AN-BA) binder that was superior to the SBR binder electrodes.

1. Introduction

Generally, polyvinylidene fluoride (PVDF) has been used as a conventional binder for lithium-ion battery (LIB) due to its superior chemical and electrochemical stabilities, however it suffers from problems such as the use of toxic organic solvents (e.g. n-methylpyrrolidone), and heat stability problems [1,2]. As a result, water-soluble or water-dispersed binders, such as carboxymethyl cellulose (CMC) [3,4], styrene-butadiene rubber (SBR) [5,6], and other water-based polymers [7,8] were successfully adopted. Much attention has been given to the synthetic SBR binder due to its high flexibility, good adhesion strength, and electrochemical stability with environmentally-friendly manufacturing process. Additionally, the SBR binder can connect the active material by a point-to-point contact mechanism such that the amount of binder used can be reduced compared to conventional PVDF binders [6].

Polyacrylonitrile (PAN) is a good choice for a binder due to its high polarity, electrochemical stability and ability to participate in Li^+ transport [9–11]. Unfortunately, PAN is a semicrystalline polymer with a high glass transition temperature (T_g) of 96.5 °C such that its application as a binder can produce a rigid electrode leading to cracking during the manufacturing process. To resolve this problem, modifying PAN with a flexible polymer through copolymerization in a water medium can be acceptable. In this work, butylacrylate (BA) is chosen as it has a very low T_g of −45 °C. The copolymerization of acrylonitrile (AN) with BA can improve the adhesion strength, electrical and electrochemical properties of electrodes [8]. Furthermore, the copolymer, poly(acrylonitrile-butylacrylate) (P(AN-BA)) has a mechanical behavior similar to synthetic acrylonitrile-butadiene rubber [12]. This study was directed to optimize AN/BA ratio in the P(AN-BA) binder and prove that P(AN-BA) is a promising binder for LIB anodes compared to commercial SBR binders.

2. Experimental

The copolymers (Fig. 1a) of AN and BA (Junsei Chemical Co., Japan) were prepared by emulsion polymerization at 70 °C. Potassium persulfate (KPS, Sigma–Aldrich) and sodium dodecyl sulfate (SDS, Tokyo Chemical Industry Co.) were used as an initiator and emulsifier, respectively. A mixture of AN/BA with different weight ratios (2/1, 1/2, 0/3) was examined as monomers for the emulsion polymerization. The 3/0 AN/BA sample, PAN, was not considered since the PAN was neither made by the emulsion polymerization mentioned below nor a water-soluble binder. SDS and an aqueous mixture of AN/BA were first stirred at room temperature for 1 h under bubbling nitrogen. A specific amount of KPS (approximately 1 part of the monomer) dissolved in water was added to the reactor after increasing the temperature to 70 °C. This step was prolonged for 4 h to complete the polymerization. The reactor was then cooled to room temperature and the emulsion was stabilized for 24 h before characterization. The particle size of the emulsion was examined using a laser diffraction light scattering technique performed by a Microtrac S3000 apparatus. The thermal stability was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a nitrogen atmosphere and 10 °C/min heating/cooling.

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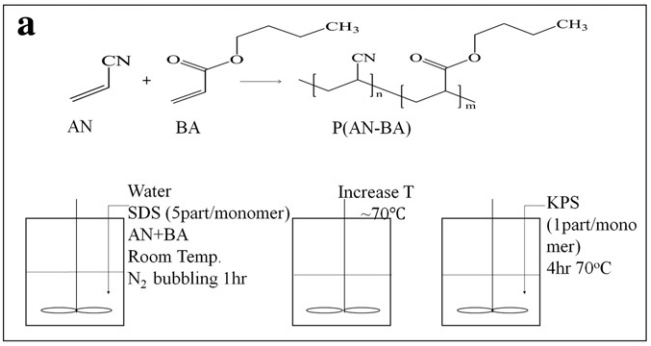

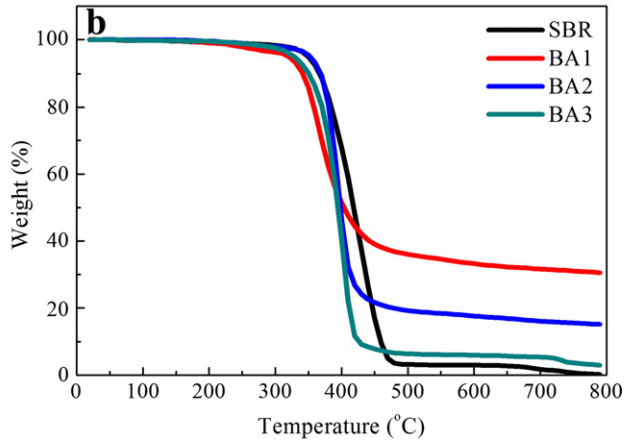

Fig. 1. (a) Chemical structures of AN, BA, and P(AN-BA). (b) Thermogravimetric analysis results of the P(AN-BA) and SBR binders.

The polymers were used as binders for LIB anodes. A typical SBR (BM-400B, Zeon Corporation, Japan) was considered as a reference binder. The electrode composition was 90 wt% graphite (GX15C, d = 10–12 μm, Carbonix Co.), 2 wt% vapor grown carbon fiber, 3 wt% CMC, and 5 wt% synthesized P(AN-BA) or SBR. Distilled water was used as a solvent for all cases. After mixing with a planetary ball mill, the slurry was coated to the 18-μm-thick Cu-foil by an automatic film-coating apparatus. The electrode thereafter was dried at 60 °C for 30 min and in a vacuum oven at 80 °C for a day to completely remove the remaining solvent before cell assembly. The loading of the electrodes was at 1.4 ± 0.1 g/cm^3. 1 M $LiPF_6$ in 1:1:1 ethylene carbonate: dimethyl carbonate:ethyl methyl carbonate by volume (Panaxetec Co., Korea) was used as an electrolyte to produce the CR2016 type coin-half cells. Lithium metal was used as a counter electrode. Additionally, cells were fabricated with a working electrode composed of only a binder film (approximately 1-μm thick) coated on Cu-foil and the electrochemical properties were characterized. Electrochemical impedance spectroscopy (EIS) with a frequency range of 100 kHz to 0.01 Hz and cyclic voltammograms (CV) of the coin-half cells at a scan rate of 0.5 mV/s within a voltage range of 0–3 V were performed by BioLogic Science Instruments. The coin cells were galvanostatically charged/discharged from 5 mV to 2.0 V in a battery test system (WBCS3000, Wonatech, Korea).

3. Results and discussion

The results in Table 1 indicate that there was not much difference in particle size between the samples synthesized via a batch process. The average size of the BA series was from 127 to 146 nm. Similarly, the total solid content and viscosity were nearly the same for these emulsions. T_g of the polymers are also in Table 1, with the lowest T_g belonging to the lowest AN/BA ratio polymer and the highest T_g belonging to the highest AN/BA ratio polymer. As expected, the flexibility of the polymer strongly depends on the amount of BA, and increasing the BA makes the polymer more flexible owing to the decrease in the amount of relatively stiff nitrile groups in AN. The BA2 sample especially showed nearly zero gel content measured by tetrahydrofuran, such that it is more flexible than any other BAs including SBR. The sample whose AN/BA ratio was 0.5/2.5 also had zero gel content (not shown here).

Table 1
Physical properties of the binder samples and the adhesion strength, the discharge capacity and initial efficiency of the electrodes containing the polymer binders.

Sample name	SBR	BA1	BA2	BA3
AN/BA	–	2/1	1/2	0/3
Particle size (nm)	98	127	146	144
T_g (°C)	−11	51	5	−45
Total solid content (%)	40	28.14	27.86	28.53
Viscosity (cP)	75	50	50	<50
Gel content (%)	78.1	95	0	89
Adhesion strength (g_f/cm)	211.7	3.5	64.9	270
Discharge capacity (mAh/g)	367	388	392	347
Initial efficiency (%)	88.8	81.9	90.9	89.8

It is clear from Fig. 1 that the thermal decomposition of the BA samples occurred at greater than 300 °C, though their weight loss was strongly affected by their compositions. Among these synthesized polymers, the BA2 sample was the most thermally stable polymer as it can stand a temperature as high as 350 °C without decomposition, just as can the conventional SBR binder.

By measuring the 180° peel strength of the graphite electrodes containing the BA samples, the adhesion capability of the BAs was investigated, as shown in Table 1. As the amount of BA in the copolymer increased, the adhesion strength increased due to the adhesive characteristics of the acrylate groups.

To examine the electrochemical stability of the BA samples, the CV and EIS of the working electrodes composed of only the BA films were performed and displayed in Fig. 2. In Fig. 2(a), CV curves of the BA2 samples showed no irreversible reactions between 0 and 3 V, except for the first reduction. The irreversibility in the first cycle may be induced from the decomposition of the electrolyte, unreacted monomers and remaining water. Similar CV curves were observed in the other BAs (not shown) and SBR samples (in Fig. 2b). Based on the EIS of the binder films and the following equation [13],

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2},$$

the diffusion coefficients of the binder for lithium ions were calculated as described inside Fig. 2(c). Compared to the SBR, the BA samples showed high diffusion coefficients due to the ether segment in acrylate, which is favorable for lithium ion diffusion. In the case of BA2, the gel content listed in Table 1 was zero, such that the ion transfer via a hopping mechanism in BA2 is relatively easier than in the other cross-linked BA binders. Other polymer configurations such as molecular weight and degree of branch also influenced the greatest diffusion coefficient of the BA2 sample [14]. Based on the EIS of the electrodes using the binders in Fig. 2(c), the electrodes containing relatively less BA content in the binder, BA1 and BA2, have lower impedance than that containing the BA3 binder. Generally, more adhesive binder covers more of the graphite surface than the low adhesive binder, leading to high resistance to lithium ion transfer through the coverage [15]. Overall, in comparison with the SBR reference sample, the water-based P(AN-BA) binders revealed reasonable and competitive impedance results, which is a key factor in battery studies.

Further electrochemical characteristics of the binder were investigated by cyclic and high rate tests, and the results are displayed in Fig. 3. In the cyclic test, shown in Fig. 3(a), the cells were charged and