



Physically cross-linked polymer binder based on poly(acrylic acid) and ion-conducting poly(ethylene glycol-co-benzimidazole) for silicon anodes



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HIGHLIGHTS

- Physically-crosslinked polymer binders are developed for Si anode.
- Physical and electrochemical properties of new binders are investigated.
- Reversible acid-base interaction and ion conductivity are provided to new binders.

GRAPHICAL ABSTRACT



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ABSTRACT

The practical applications of Si electrodes in lithium-ion batteries are limited since they undergo large changes in volume during charge and discharge, and consequently become highly deteriorated. A novel binder system holding silicon particles together and preventing disintegration of the electrode during operation hence needs to be developed to enable reliable cycleability. In the current work, such a new polymer binder system, based on poly(acrylic acid) (PAA) and poly(ethylene glycol-co-benzimidazole) (PEGPBI), is developed for silicon anodes. The physical crosslinking using acid-base interactions between PAA and PBI, together with the ion-conducting PEG group, yields physical properties for the resulting PAA-PEGPBI-based anodes that are better than those of electrodes based on the currently available PAA binder, and yields good cell performances. A Si-based electrode with high loading levels of $1.0-1.3 \text{ mg cm}^{-2}$ ($0.7-0.91 \text{ Si mg cm}^{-2}$) is reliably manufactured using specifically PAA-PEGPBI-2, which is made with 2 wt% of PEGPBI relative to PAA, and shows a very high capacity value of 1221 mAh g^{-1} at a rate of 0.5 C after 50 cycles, and a high capacity value of more than 1600 mAh g^{-1} at a high rate of 2 C.

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1. Introduction

The use of fossil fuels is causing serious environmental problems such as global warming. Therefore, alternative efficient energy systems have been developed to reduce the use of fossil fuels, and lithium-ion secondary batteries, in particular, have become an

increasingly important subject of investigation as large-scale energy storage devices in applications such as electric vehicles and energy storage systems [1–4]. However, the currently available lithium-ion secondary batteries, which use LiCoO_2 and graphite as the active materials, do not have sufficiently high energy density levels to efficiently power the aforementioned high energy-demanding applications.

Recently, to solve these problems, a variety of alternate electrode materials have been studied, and among them, Si has received much attention as a prospective anode material because it

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is an environmentally friendly material and its electrodes have shown large capacity levels of up to 4200 mAh g⁻¹ [5–9]. However, Si electrodes are not dimensionally stable, as their volumes change by more than 400% when the Si is lithiated to Li_{4.4}Si. Mechanical stresses occurring during these repetitive processes damage the anode, induce separation of its components, isolate Si particles having insulation properties, and ultimately cause rapid deterioration of the battery system [9–12].

Thus, many researchers are now focused on developing a strong polymer binder that can endure large volume changes and prevent electrodes from becoming ruptured. It has been reported that polymers with many hydrophilic functional groups such as poly(vinyl alcohol) (PVA) [13,14], poly(acrylic acid) (PAA) [15–17], carboxymethyl cellulose (CMC) [18,19] and polysaccharides [20,21] can be used to increase the lifespan of Si anodes because they have good physical properties as a result of their strong interactions with OH groups on silicon particles, and these polymers may thus substitute for the currently used polyvinylidene fluoride (PVDF) binder. In addition, cross-linkages involving chemical bonds such as covalent bonds [17,22,23] or even cross-linkages involving physical interactions such as hydrogen bonds [24–26] have been used to further enhance the physical properties of these polymer binders and to greatly improve cell performance.

Recently, we reported a new polymer binder material based on the acid-base interaction [27]. In that work, we produced a reversible physical cross-linkage by adding basic polybenzimidazole (PBI) to acidic functional groups of PAA. The degree of crosslinking was easily controlled by adjusting the amount of crosslinking agent (PBI) added, and the mechanical properties of an Si electrode and the overall cell performance improved by adding a small amount of the PBI crosslinking agent to make a PAA-PBI blend. The PBI cross-linker, however, is poorly soluble, due to the rigidity of its structure, making it difficult to prepare electrodes with high loading levels from this PAA-PBI polymer blend.

We have now combined PBI with poly(ethylene glycol) (PEG), with the PEG used both as a solubilizing and ion-conducting group, to prepare the cross-linker PEGPBI. The added PEG moiety was thought to improve the flexibility and solubility of the PBI polymer, as well as to endow this cross-linker with the ability to conduct ions. The use of the PAA-PEGPBI blend as a polymeric binder hence made the manufacturing of Si electrodes with a higher loading level possible, and the cell prepared from this Si anode displayed good performance.

2. Experimental

2.1. Materials

Poly(ethylene glycol) ($M_r = 600$) and poly(acrylic acid) ($M_w = 450,000$) were obtained from Aldrich Chemical Co. 3,3'-Diaminobenzidine was obtained from TCI. All the other chemicals were obtained from commercial sources and used without further purification. The Super P was provided from Korea Electronics Technology Institute (KETI), Korea.

2.2. Synthesis of the poly(ethylene glycol)-poly(benzimidazole) (PEGPBI) (1)

2.2.1. Synthesis of the carboxylic acid-terminated poly(ethylene glycol) (PEG-COOH) (2)

Poly(ethylene glycol) (3 g, 5 mmol) with magnetic bar was placed into a round-bottom flask. Then 0.16 M chromic acid solution (60 cm³) was added. The reaction mixture was stirred at room temperature for 12 h. Chloroform was added and the phases were separated, the organic phase was dried over Na₂SO₄ and the solvent

was evaporated to give the PEG-COOH (2) (1.8 g, 57%) as colorless liquid; δ_H (400 MHz, CDCl₃), 9.70 (2H, s, -COOH), 4.15 (4H, s, -OCH₂COOH), 3.7–3.6 (44H, br signal, -OCH₂CH₂O-); δ_C (400 MHz, CDCl₃), 172.0 (-COOH), 70.0 (-OCH₂COOH), 61.0 (-OCH₂CH₂O-); ν (CHCl₃)/cm⁻¹ 3010, 2867, 1727, 1342, 1214, 1093.

2.2.2. Synthesis of poly(ethylene glycol-co-benzimidazole) (PEGPBI) (1)

PEG-COOH (2) (1 g, 1.592 mmol) was dissolved in a concentrated HCl (5 cm³) solution, to which a 3,3'-diaminobenzimidine (0.341 g, 1.592 mmol) solution in concentrated HCl (5 cm³) was then added. This reaction mixture was stirred at 150 °C for 40 h and then cooled down in an ice bath. The resulting mixture was neutralized with an 8 N NaOH solution until the pH became 6 and then stirred for 15 min. To the subsequent mixture, 3 M sodium bicarbonate was added until the pH became 9, and the resulting mixture was stirred for 2 h. Finally, the product was washed with deionized (D.I.) water and centrifuged several times to give PEGPBI (1) (0.3 g, 22%) as a black glassy solid; δ_H (400 MHz, CD₃OD) 7.80 (s, NH), 7.65 (m, ArH), 7.45 (m, ArH), 6.9 (m, ArH), 4.8 (s, -NCC₂H₂O-), 3.8–3.4 (br signal, -OCH₂CH₂O-).

2.3. Fabrication of the Si nanoparticle (SiNP) electrode

To make a SiNP electrode, silicon nanoparticle (Alfa Aesar, 0.175 g), PAA ($M_w = 450,000$, 0.025 g) and conductive carbon (Super P, 0.050 g) were dispersed in NMP with a SiNP:PAA:conductive carbon mass ratio of 7:2:1. The PAA-PEGPBI binder solutions were prepared by dissolving PAA (0.70 g) in NMP (5 cm³) and dissolving PEGPBI (7.07 mg for the PAA-PEGPBI-1-based electrode (see below), 14.28 mg for PAA-PEGPBI-2, and 77.8 mg for PAA-PEGPBI-10) in NMP and then mixing these two solutions thoroughly before making the PAA-PEGPBI-based electrodes. Then the concentration of the PAA-PEGPBI binder in each binder solution was adjusted to 0.122 g of binder per gram of solution. A mixture of SiNPs and conductive carbon was then dispersed into each binder solution with a SiNP:conductive carbon:binder mass ratio of 7:2:1. In each case, the resulting slurry was coated onto a Cu foil. As-formed electrodes were dried under vacuum at 140 °C for 6 h. The loading of the active materials for all electrodes was fixed at 0.7–0.91 Si mg cm⁻².

2.4. Characterization and measurements

¹H NMR spectra were obtained from an Agilent 400-MR (400 MHz) instrument using CDCl₃, DMSO-*d*₆ or CD₃OD as a reference or using an internal deuterium lock. FT-IR spectra were recorded on a Varian 640-IR spectrometer. Scanning electron microscopy (SEM) was performed using a JEOL JSM-7800F instrument and using electrodes washed in dichloromethane. X-ray photoelectron spectroscopy (XPS, Al K α) experiments were carried out on a PHI 5000 VersaProbe II instrument with a chamber pressure of 1×10^{-9} torr. The source power was set at 25 W. Survey scans were carried out in an 1100-0 eV binding energy range with 0.4 eV steps and a dwell time of 20 ms. Narrow high-resolution scans were run with 0.2 eV steps and 20 ms dwell times.

2.5. Peel test

To determine the level of adhesion of each binder, prepared electrodes were cut into 10 mm-wide, 50 mm-long rectangular shapes and attached to 3 M tape. The peel strength of each electrode specimen was recorded with a universal testing machine (Shimadzu EZ-L). By pulling the tape at a constant displacement rate of 60 mm min⁻¹, the applied force was continuously measured

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