



The existence of optimal molecular weight for poly(acrylic acid) binders in silicon/graphite composite anode for lithium-ion batteries



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HIGHLIGHTS

- Molecular weights (MWs) of PAA binders were characterized using a standard protocol.
- Their properties were elevated and correlated to MWs.
- 15 wt% Si electrodes were used to evaluate the cycling performance of those binders.
- A Mn range of 24–150 kDa is suggested to achieve optimized performance.

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ABSTRACT

Poly(acrylic acid) (PAA) based binders have been widely used for the high capacity silicon anodes of lithium-ion batteries. While numerous promising progress has been reported, there is no general guideline for choosing the right PAA binders for optimized cycling performance. In this report, aiming to optimize the cycling performance of the Si/graphite composite anodes (15 wt% Si), we systemically investigated a series of PAA binders by validating their molecular weights (MWs) and correlating them to the cycling performance of the anodes fabricated with such binders. The gel permeation chromatography (GPC) was used to validate the MWs of six PAA binders (PAA1 to PAA6). Those binders then underwent a series of characterizations, including rheology study, half-cell cycling, scanning electron microscope (SEM), and Fourier-transform infrared spectroscopy (FTIR). It is observed that the MWs of PAA binders not only affected the viscosities of the binder solutions but also impacted the cycling performance, possibly due to the cohesion changes. A range of 24–150 kDa is found to be optimal for minimizing the rate and extent of capacity fade and maintaining the cohesion in the electrode matrix despite the dramatic volumetric changes due to Si alloying.

1. Introduction

Due to its excellent cyclability and low cost, graphite serves as an anode material of choice in commercial lithium-ion batteries (LIBs). However, the low specific capacity of this material (372 mAh/g) circumscribes its use in high energy batteries [1]. Silicon has a higher theoretical specific capacity of ~4200 mAh/g and relatively low cost, so it is considered as a promising replacement of graphite in the next generation LIBs [2]. However, Si anodes have poor cycling behavior stemming from large expansion (~300 vol%) of Si particles during their Li alloying in the lithiation stage and the corresponding contraction upon delithiation that together lead to particle pulverization, electrode delamination, and destabilization of solid-electrolyte interphase (SEI) on the particle surface, leading to the formation of the pore-

filling deposits, drying of the electrolyte, and densification of the electrode matrix [3]. Polymeric binders that are added to the matrix to provide cohesion between the Si particles and conductive carbon particles need to prolong the structural integrity of the electrode matrix (maintaining cohesion and electric conduction between the particles) despite these detrimental structural and compositional changes. Several polyol and/or polycarboxylate polymers have been reported to-date that partially accomplish this task, including poly(vinyl alcohol), carboxymethyl cellulose, alginate and, in particular, poly(acrylic acid) (PAA) [4–7]. It is believed that such binders form covalent links to siloxyl (SiOH) groups present at the surface of the SiO₂ layer around the active Si particles [4]. In this fashion, the Si particles remain linked to the polymer binder during their cycling thereby maintaining the cohesion in the matrix despite the enormous volumetric changes.

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Most of these polymer binders are commercial products developed for other uses, and there is insufficient understanding of factors controlling their performance in Si-based negative electrodes. In addition to low cost, excellent surface binding and improved stability [6], the PAA binders are also water-soluble, which allows “green” fabrication that is currently favored by the industry and regulators. While this polymer material is available in a variety of molecular weights (MWs) [8,9], currently there is no science-based guidance for choosing a particular PAA brand. We note that MW of a polymer is one of the most important factors controlling its physicochemical properties, such as viscosity, stiffness, adhesion strength, etc. [10] We also note that PAA has been used as a constituent in block copolymer binders (that can integrate more than one kind of active materials); the development of such binders is hindered by lack of knowledge of the optimal size of the Si-binding PAA domains [11–16].

In this report, we aim to understand how MW of PAA binder influences cell performance of Si/graphite composite electrodes. Such electrodes contain only ~15 wt% Si to reduce the overall expansion of the electrode during lithiation (the expansion of the lithiated graphite is only 11 vol%); both graphite and silicon serve as active materials in these composite electrodes.

2. Experimental section

2.1. Materials

Poly(acrylic acid) (PAA) with different nominal MWs, denoted as PAA1 to PAA6, were purchased from Sigma-Aldrich, Polysciences and Acros (see Table 1 for more detail). PAA with ultra high MW ($M_v \sim 3000$ kDa, Sigma Aldrich) was also tested, however, it's aqueous solution is very viscous even at low concentration (3 wt%) and thus almost impossible to use this PAA aqueous solution to cast the laminate. Therefore it will not be discussed in this paper. A methylation agent, trimethylsilyldiazomethane (2.0 M solution in *n*-hexane, Sigma-Aldrich), was used as received. Silicon particles (70–130 nm) were purchased from NanoAmor; graphite flakes MagE were obtained from Hitachi; conductive carbon particles (C45, 50–60 nm) were purchased from Timcal. Gen 2 electrolyte, which is 1.2 M LiPF₆ in a liquid mixture of ethylene carbonate and ethyl methyl carbonate (3:7 by weight), was provided by Tomiyama Pure Chemical Industries. Fluoroethylene carbonate (FEC) used as SEI building additive was purchased from Solvay.

2.2. General characterization

To make it more compatible to the nonaqueous system of the gel permeation – size exclusion chromatography (GPC/SEC), PAA was first quantitatively converted to poly(methylacrylate) (PMA, see below). The elution of PMA in tetrahydrofuran (THF) was carried out at 1 mL/min and 30 °C using an Agilent 1260 Infinity II GPC/SEC chromatograph with a refractive index detector. A PLgel 5 μ m guard column and

Table 1
Molecular weights (in kDa) and polydispersity indices (PDI) of PAA samples 1 to 6.

Sample	Vendor	MW ^a	M _n ^e	M _w ^e	M _v ^e	PDI ^e
1	Aldrich	450 ^b	167	964	784	5.78
2	Aldrich	250 ^c	36	124	105	3.43
3	Aldrich	130 239.3 ^d	147	713	588	4.86
4	Polysciences	50	24	76	66	3.11
5	Acros	5	3.0	5.7	5.2	1.89
6	Polysciences	2	1.6	2.5	2.3	1.57

^a Vendor specifications.

^b M_v.

^c M_w.

^d M_n.

^e Our GPC/SEC measurements.

three PLgel 5 μ m mixed-B columns (Agilent) were used in combination. Narrow-dispersed polystyrene standards (Agilent EasiVial PS-M) were used for calibrations, and the data were processed using Cirrus GPC/SEC software.

Rheological measurements were carried out using a TA Instruments rheometer (Model TA AR 2000ex) in a cone-plate geometry with a cone diameter of 20 mm and an angle of 2° (truncation 52 μ m); the temperature (25 °C) was controlled by the bottom Peltier plate. To minimize water evaporation during these measurements, the solvent trap was filled with water, and a solvent trap cover was used. Dynamic storage modulus G' was measured in a time sweep experiment and the apparent viscosity as a function of shear rate was measured in a continuous ramp.

2.3. Methylation of PAA for GPC test

The PAA samples were converted to PMA using trimethylsilyldiazomethane in dry hexane as a methylating agent [17]. The excess amount of this reagent was added into a PAA solution in a mixture of water and THF (1:2 v./v) until the color of the solution turned yellow, and the solution was stirred for 3 h. A gentle flow of nitrogen removed the solvent from a weighted aliquot. Quantitative methylation was confirmed using proton NMR spectroscopy (nuclear magnetic resonance spectra were obtained using a Bruker DPX-300 spectrometer). PAA (δ in CD₃OD, chemical shift δ in ppm vs. tetramethylsilane): 1.24–2.77 (w, backbone); PMA (δ in CDCl₃): 3.65 (s, -COOCH₃), 1.20–2.48 (w, backbone).

2.4. Silicon/graphite composite electrode

PAA binders were dissolved in deionized water and titrated using LiOH to pH ~6–7 in order to obtain lithiated PAA (LiPAA). The electrode contained 73 wt% graphite flakes, 15 wt% Si particles, 2 wt% C45 and 10 wt% LiPAA. The active material loading was ~3 mg/cm². Before cell assembly, the electrodes were dried in a vacuum oven at 80 °C for 8 h. Electrochemical performance was evaluated in 2032-type coin cells. The cells were configured with a lithium metal electrode, a microporous polypropylene separator (Celgard 2325), a Si/graphite composite electrode, and an appropriate amount (50 μ L) of Gen 2 electrolyte containing 10 wt% FEC. The cells were first subjected to three formation cycles at C/20 rate and then 100 cycles at C/3 rate with the cell voltage maintained between 0.01 V and 1.5 V during this cycling.

2.5. Post-cycling analysis

For the post-cycling analysis, the cells were disassembled in the inert atmosphere; the electrodes were thoroughly rinsed with anhydrous dimethyl carbonate and dried in a vacuum oven. The morphologies of the pristine and cycled electrodes were examined using a FEI Quanta 400F scanning electron microscope. Fourier-transform infrared (FTIR) spectra of these electrodes were obtained using a Thermo Scientific Nicolet iS5 spectrometer [18,19].

3. Results and discussion

Table 1 summarizes MWs for our six PAA polymers and they are numbered based on their MWs as provided by the vendors with PAA1 being the largest. To characterize their materials, the manufacturers use different methods with different MW quantities being used, including the number average MW (M_n), the weight average MW (M_w), and the viscosity average MW (M_v), which could cause huge confusions due to their widely varied values for the same material. Due to such inconsistent practice and great dispersity of synthetic polymers, it is difficult to compare different materials using the specifications provided, so a standardized GPC/SEC method of MW characterization was used to

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