



What makes lithium substituted polyacrylic acid a better binder than polyacrylic acid for silicon-graphite composite anodes?

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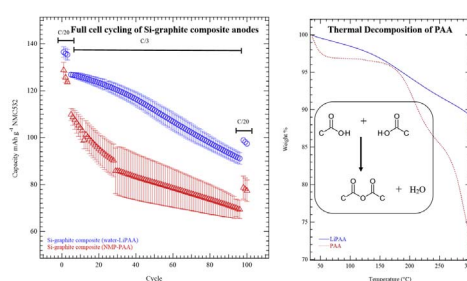
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HIGHLIGHTS

- Practical Si-graphite composite electrodes were produced with PAA or LiPAA binders.
- Full cells prepared with LiPAA based electrodes perform better than PAA.
- PAA Si-graphite composites' full cell performance varies with drying temperature.
- PAA Si-graphite electrodes are more hydroscopic than the LiPAA counterparts.
- PAA is reduced to LiPAA during cycling, resulting in poor Coulombic efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium substituted polyacrylic acid (LiPAA) has previously been demonstrated as a superior binder over polyacrylic acid (PAA) for Si anodes, but from where does this enhanced performance arise? In this study, full cells are assembled with PAA and LiPAA based Si-graphite composite anodes that dried at temperatures from 100 °C to 200 °C. The performance of full cells containing PAA based Si-graphite anodes largely depend on the secondary drying temperature, as decomposition of the binder is correlated to increased electrode moisture and a rise in cell impedance. Full cells containing LiPAA based Si-graphite composite electrodes display better Coulombic efficiency than those with PAA, because of the electrochemical reduction of the PAA binder. This is identified by attenuated total reflectance Fourier transform infrared spectrometry and observed gassing during the electrochemical reaction. Coulombic losses from the PAA and Si SEI, along with depletion of the Si capacity in the anode results in progressive underutilization of the cathode and full cell capacity loss.

1. Introduction

There is interest in exploring high capacity anode materials that can be paired with cathodes, such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x + y + z = 1$), to achieve high energy batteries. Of the potential anode materials, Si one

of the most extensively researched because of its high gravimetric capacity of 3579 mAh g^{-1} , upon formation of $\text{Li}_{15}\text{Si}_4$ intermetallic [1]. Moving to Si from more conventional graphite anodes would allow for drastically lighter and thinner anodes to match the equivalent cathodes. That said, Si anodes with higher loadings have a number of issues

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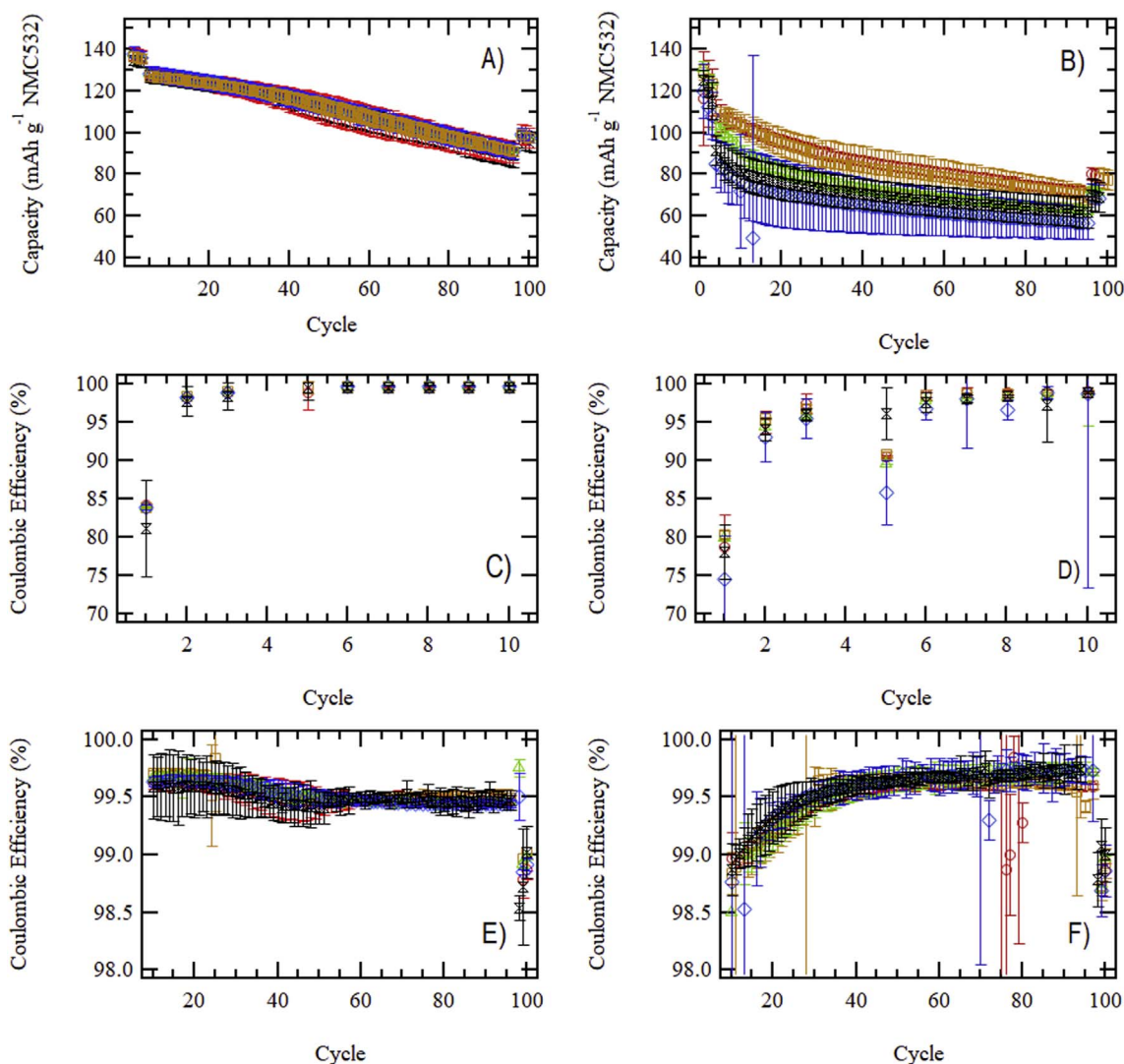


Fig. 1. Cycle life of A) LiPAA full cells and B) PAA full cells. The Coulombic efficiency for the first 10 cycles of C) LiPAA full cells and D) PAA full cells. The long term Coulombic efficiency of E) LiPAA full cells and F) PAA full cells. The secondary drying temperature of the Si-graphite composite anodes are 120 °C (red circle), 140 °C (gold square), 160 °C (green triangle), 180 °C (blue diamond), and 200 °C (black hour glass). Each point is an average of 3 cells. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

related to large volumetric expansion accompanied by the Li alloying [2]. Dispersion of Si within a graphite matrix has proven to be an effective strategy to maximize both capacity and cycle life in these materials [3]. This method is a simple way to minimize volumetric expansion and agglomeration of the Si in a fashion that can be easily incorporated into traditional roll-to-roll manufacturing techniques.

A crucial component of these Si-graphite composite electrodes is the binder which plays an important role in particle-particle cohesion and particle-current collector adhesion. Traditionally polyvinylidene fluoride (PVDF) has been utilized for graphite based electrodes, but this binder proves ineffective with the large volumetric expansions of Si [4]. Alternatively, binders such as Na-carboxymethyl cellulose (CMC) [4], Na-alginate [5], and poly acrylic acid (PAA) [6] show improved capabilities in Si based systems. These binders all have large quantities of hydroxyl or carboxylic acid groups that are thought to interact with the surface oxide of Si. Further improvements have been established by neutralizing the acidic protons of PAA with LiOH, forming LiPAA, with an average Li substitution of 80% [7]. Doing so may unbundle the polymer chains and possibly improve interactions with the Si surface due to the negatively charged carboxylate [8]. LiPAA has been proposed to have Li⁺ conductivity, though no evidence has been produced supporting this claim [7,9].

LiPAA also has some undesirable features as a binder. From a mechanical standpoint PAA films are, qualitatively, more flexible than LiPAA films. We observe that 1 mm thick LiPAA films easily break when flexed between two hands, while similar PAA films can withstand more stress, though quantitative values must still be obtained. PAA also benefits from solubility in *N*-methyl-2-pyrrolidone (NMP) or water, LiPAA is only soluble in water. This is beneficial as the elimination of NMP in these slurries would allow for a more environmentally friendly means of production [10]. However, it is still unclear if water based slurries are feasible for Si, as addition of water may lead to further surface oxidation [11,12].

With these additional considerations in mind the question still stands: why does LiPAA perform better than PAA as a binder for Si anodes? Differences in these binders are investigated using Si-graphite composite electrodes, which are implemented in full cells with LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ cathodes. Secondary drying is optimized to minimize residual water while addressing degradation pathways of PAA and LiPAA. Furthermore, correlations between the electrochemical stability of these binders and the Coulombic efficiency of the related Si-graphite anodes are linked to observed gas formation.

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