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Understanding why poly(acrylic acid) works: decarbonylation and cross-linking provide an ionically conductive passivation layer in silicon anodes†

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Poly(acrylic acid) (PAA) is commonly used as a binder for fabricating silicon (Si) anode active materials in lithium-ion batteries due to its useful properties including high polar solvent solubility, good rheology, and strong adhesive properties. However, the role and evolution of PAA during electrode fabrication, cycling, and calendar aging are not well understood. In this work, we reveal the evolution of PAA during electrode curing and relate its chemical change to the final electrode properties and performance. These studies are made possible using two types of *in situ* attenuated total reflectance-infrared Fourier transform (ATR-FTIR) spectroscopy: thermal ATR-FTIR to probe the cross-linking reaction, and ATR-FTIR spectroelectrochemistry of three-dimensional composite electrodes, a unique technique developed herein that probes the solvation dynamics of lithium ions at the silicon anode interface under electrochemical polarization. Specifically, we show that PAA undergoes a thermally-mediated, cross-linking decarbonylation reaction to form an ether-based network polymer. To show the importance of the polyether moieties, we synthesize partially esterified PAA analogues that do not undergo this cross-linking decarbonylation reaction and correlate the degree of cross-linking to half-cell performance metrics. Finally, we unveil the mechanism of the polyether binder performance through *in situ* ATR-FTIR spectroelectrochemistry and show that PAA acts as an interfacial material that conducts lithium-ions, limits solvent molecule access to the Si surface, and stabilizes the electrode against parasitic lithium inventory loss at high state of charge for an extended period of time.

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Introduction

Poly(acrylic acid) (PAA)-based binders are ubiquitous in composite electrodes in lithium-ion batteries (LIBs). High silicon (Si) content LIB anodes have received considerable interest recently as a promising technology to significantly boost LIB energy densities.^{1,2} However, Si suffers from detrimental large volume change during lithiation and the presence of unstable surface species.¹ Several reports have examined how various polymeric binders (including PAA and others) impact the mechanical stability and cycling performance of silicon anodes.^{3–7} Other work has shown that binder chemistry also plays an important role in dictating slurry properties,^{8,9} final electrode morphology,^{10,11} and the overall performance of Si anodes.^{12,13} In addition, significant advances have been made in device performance by implementing new structural variations

of PAA and other carboxyl-containing polymers.^{14–17} Other investigations have taken this concept one step further by tailoring Si nanoparticle (NP) surface chemistry to covalently link polymeric binders to the Si NP surface.^{18,19} Given this body of literature, it is now well-understood that binders can experience a variety of chemical and structural evolutions during slurry processing and electrode curing that can influence the interfacial chemistries that lead to the solid electrolyte interphase (SEI).

Despite these significant improvements in electrochemical performance, the dynamic nature of interfacial binder chemistry for composite Si anodes remains incompletely understood. For example, the various roles binders play as conformal layers that coat silicon nanoparticles,¹⁰ that react with electrolyte molecules,^{20,21} impact SEI formation,^{13,22} and influence ionic conductivity¹⁴ have all made decoupling these interrelated effects particularly challenging for Si anodes.^{23–28} This work aims to build on previous efforts to further elucidate the role and evolution of PAA interfacial coatings during electrode fabrication, cycling, and long-term voltage holds. We introduce systematic variations in the chemical structure of PAA and

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