Characterization of Annealing-Induced Phase Segregation in Composite Silicon Anodes for Li-ion Batteries

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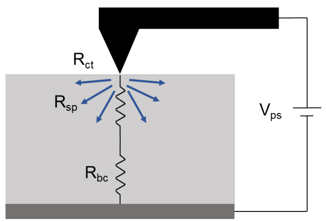
Abstract

- Silicon (Si) anodes have a greater specific capacity as compared to. graphite anodes for lithium-ion batteries (LIBs)
- Si undergoes large volumetric changes during lithiation that results in an unstable solid-electrolyte interphase (SEI)
- Electrodes made with Si nanoparticles (NPs) treated with polyethylene oxide (PEO), conductive carbon NPs, and P84 polyimide binder show significant impacts of annealing treatment on cycling
- We imaged through electrode thickness using scanning spreading resistance microscopy (SSRM), contact resonance-force volume (CR-FV), and scanning electron microscopy-based energy dispersive x-ray spectroscopy (SEM-EDS).
- Results show that the Si and conductive carbon segregate into phases with a distinctive carbon-rich banded morphology that surrounds the Si-rich phase during annealing
- These structures, as well as distinct electronic and mechanical properties, remain during cycling, suggesting an improvement of electrical conduction pathways and a mechanical strain buffer for active Si material expansion

Scanning Spreading Resistance Microscopy

SSRM is a scanning probe technique that measures composite electrode components with nanometer-scale resolution, making it ideal for distinguishing anode components and determining their spatial positions.

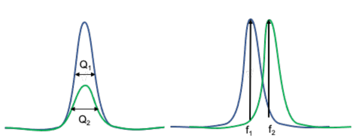


R_{ct}: tip contact resistance
R_{sp}: spreading resistance
R_{bc}: back contact resistance

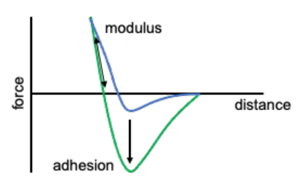
$$R_{sp} = \frac{V_{ps}}{I}$$

$$\rho = 4 * r_{tip} * R_{sp}$$

Contact Resonance and Force Volume



Contact resonance (CR) measures the change in resonant frequency of the probe when it contacts the sample to get mechanical properties



Force volume (FV) measures the. shape of the force-distance curve of the probe as it contacts the sample to get mechanical properties

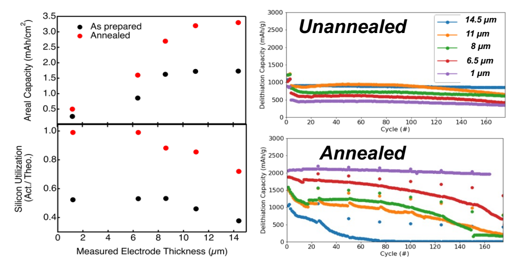
Samples Studied

Electrode Composition:
80% 5.9nm PEO-treated Si (made by plasma-enhanced chemical vapor deposition, 78% Si by mass)
10% Ensinger P84
10% Timcal C45

Full Cell Cycling (Coin cell):
Preformed in half-cell (3 x C/20)
NMC electrodes provided by CAMP
4.2 – 3.0V
Gen2+3% FEC electrolyte

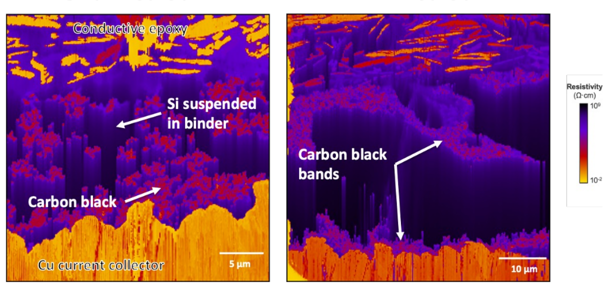
Samples:
- Pristine unannealed
- Pristine annealed
- Cycled 25x unannealed
- Cycled 25x annealed

Electrochemical Improvement with Annealing



Annealing improves capacity and silicon utilization, but these gains diminish as electrode thickness increases.

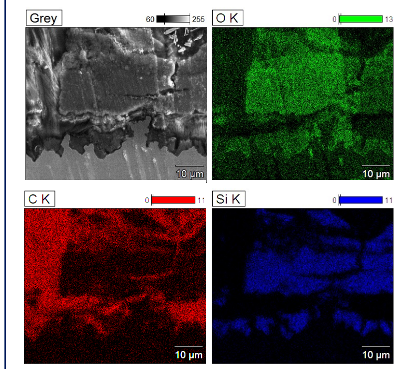
Phase Segregation in Pristine Electrodes



SSRM resistivity maps for pristine unannealed and annealed electrode cross sections.

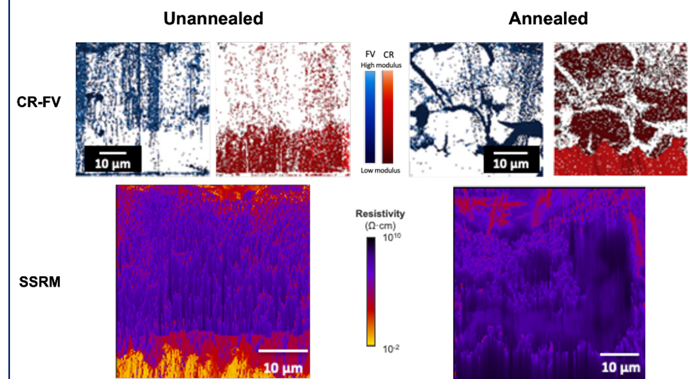
- **Unannealed:** uniform distribution of carbon black silicon particles
- **Annealed:** carbon black segregates from silicon into band-like structures

Phase Segregation in Cycled Electrodes



Energy dispersive spectroscopy (EDS) maps of annealed cycled electrode.

- Phase segregation is present after cycling
- Distinct domains in both resistivity and modulus are see in annealed cycled electrodes
- *Improved electronic pathways?*
- *Relief of strain from silicon expansion?*



Conclusions and Future Work

- Annealing PEO-treated Si electrodes causes improvement in early cycling and phase segregation
- Phase segregation remains after cycling
- Phase segregation results in distinct resistivities and mechanical properties, which may improve cycling
- Further investigation of polyimide binder is required to fully understand this segregation effect

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