Nanoscale Three-Dimensional Imaging of Degradation in Composite Si-Containing Anodes

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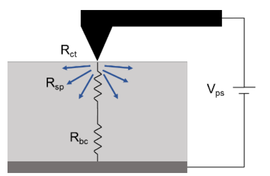
Abstract

The use of silicon (Si) in next-generation lithium-ion battery (LIB) anodes has the potential to dramatically improve electrochemical performance over current LIB graphite (Gr) anodes, due to silicon's higher specific capacity.[1] However, widespread implementation of Si-containing anodes is inhibited by issues such as significant Si volume expansion during lithiation and an unstable solid-electrolyte interphase (SEI), resulting in unreliable performance and poor cycle life. Currently, composite anodes with both Si and graphite active materials are used to increase capacity and mitigate some of the limitations associated with Si. In composite electrodes with a heterogeneous distribution of components with varying electrical properties (including Si, Gr, conductive carbon additive, and binder), it is important to understand the local distribution of each component to correlate with electrochemical processes, particularly localized degradation and heterogeneous aging, and to optimize performance.

To investigate Si-containing composite anodes in the nanoscale, we use scanning spreading resistance microscopy (SSRM), a form of scanning probe microscopy (SPM) that probes local electronic resistivity. By examining the intrinsic electronic resistivity contrast between the anode components, separate phases can be distinguished and understood within the composite structure.[2] This work studies the effect of electrochemical cycling in two different electrolytes on component distribution and aging by comparing the electrical and structural evolution of composite Si-graphite electrodes and SEI before and after charge-discharge cycling.

Scanning Spreading Resistance Microscopy

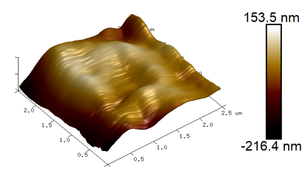
SSRM measures the local resistivities of composite electrode components over a wide range of relative intrinsic resistivities with nanometer-scale resolution and a smaller sampling volume than X-ray based methods, making it ideal for distinguishing anode components and determining their spatial positions.



R_{ct}: tip contact resistance
R_{sp}: spreading resistance
R_{bc}: back contact resistance
V_{ps}: voltage between sample and probe

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

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



AFM topography image of a crater left in electrode after milling is completed.

The probe tip mills away layers of material while also measuring the resistivity of those layers. Using Python linear interpolation across these layers, we create 3D volumes to map the resistivity of each electrode component material.

Electrodes and Electrolytes Studied

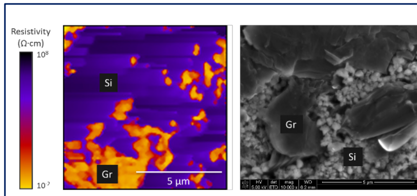
Samples are Si-Gr anodes (CAMP A-A013) in three conditions:
1. Pristine,
2. Cycled in Gen2 electrolyte, and
3. Cycled in GenF electrolyte.

Electrodes were cycled 25 times in a coin cell and left in the delitihiated state.

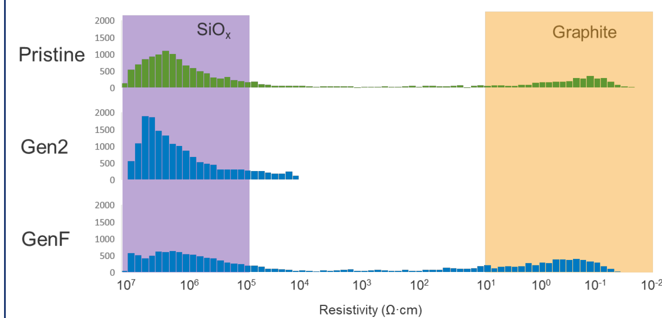
Anode composition:
- 15 wt% silicon oxide (avg. diameter 150 nm)
- 73 wt% graphite (avg. diameter 20 μm)
- 2 wt% conductive carbon
- 10 wt% lithium polyacrylate binder

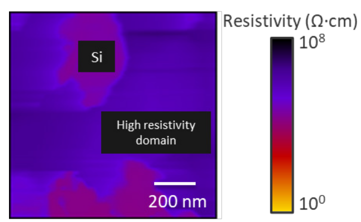
Electrolyte compositions
- Gen2: 1.2M $LiPF_6$ in EC:EMC (3:7 by wt%)
- GenF: Gen2 electrolyte + 10 wt% FEC

Electrode Component Identification



Domains in SSRM maps were identified using SEM-EDS, particle sizes, and known resistivity values[2]. Documented resistivity ranges are overlayed on resistivity histograms for each sample, below.





There are distinct higher resistivity domains in regions surrounding Si and Gr. The resistivity values measured in each of these domains were used to threshold the high resistivity volumes.

Summary and Conclusion

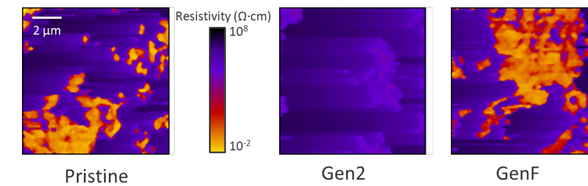
- Both 2D and 3D images of Gr, Si, and high resistivity regions of composite electrodes cycled in Gen2 and GenF electrolytes show that the sample cycled in GenF has a less of a high resistivity domain.
- Additionally, it was shown by thresholding the high resistivity domains that they do not exist only on the electrode surface but interpenetrate into the bulk of the electrode.
- Future 3D SSRM work will study the high resistivity domains as a function of cycle history, as well as degradation mechanisms, such as loss of electron transfer pathways and non-uniform lithiation by correlation morphological changes to resistivity evolution.

References

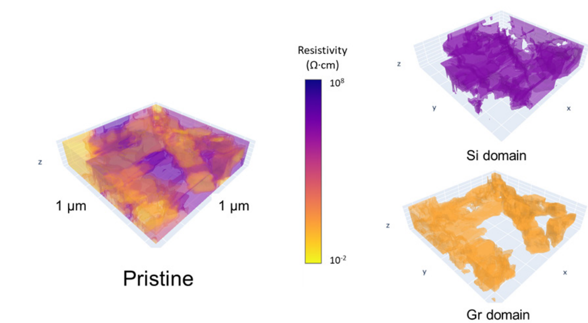
1. W. J. Zhang. A review of the electrochemical performance of alloy anodes for lithium-ion batteries *J. Power Sources* **196** 13–24 (2011)

2. C. Stetson, Z. Huey, A. Downard, Z. Li, B. To, A. Zakutayev, C.-S. Jiang, M. Al-Jassim, D. Finegan, S.-D. Han and S. DeCaluwe: Three-Dimensional Mapping of Resistivity and Microstructure of Composite Electrodes for Lithium-Ion Batteries. *ACS Nano Letters* **Accepted** (2020).

Electrode Evolution During Cycling

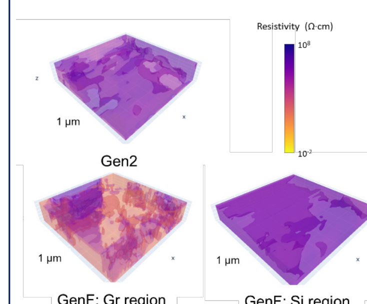


Multiple scans at random locations demonstrate that the GenF-cycled Si-graphite anodes had regions of surface graphite exposed, but Gen2 does not.

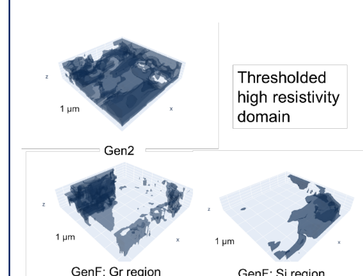


By interpolating a series of SSRM maps, 3D volumes of both the full region and of component domains were generated.

Determining exact depth of the 3D volumes is challenging due to surface roughness, but it is on the scale of 100 nm.



Regions containing Gr and Si were examined in the GenF electrode.



The high resistivity domain in both electrodes is distributed throughout the studied volume, reflecting the particulate nature of composite electrodes and the expansion and contraction that occur during cycling.

The high resistivity domain in the GenF sample is significantly less complete, more dispersed and thinner as compared to the Gen2 sample.

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