Experiment Brief

K3 IS Camera

Title

Dynamic *in-situ* lithiation of NiS-filled carbon nanotubes

Gatan Instrument Used

K3® IS camera delivers simultaneous **low-dose imaging via real-time electron counting**, fast continuous data capture, and **a large field of view**.

Background

Energy storage applications need advanced anode materials to replace graphite for improved charge storage capacity and performance. Nickel sulfide (Ni_3S_2)-filled carbon nanotubes (CNTs) have been proposed as an anode material that is a good metallic conductor for improved capacity and enhanced ion conduction due to nanostructuring of the material. Although bulk electrochemical testing has demonstrated good performance of these anodes for lithium cycling, the lithiation and deformation mechanisms are not well understood.

Materials and Methods

Ni_3S_2-filled CNTs were synthesized on a silicon substrate. The nanowires were scraped from the substrate with a razor blade, then affixed to an Al wire using conductive epoxy. The sample was loaded in a Nanofactory STM-TEM vs. Li metal on a tungsten probe and then observed in a Titan ETEM. The lithiation and deformation mechanisms were visualized using a K3 IS camera. The camera captured a series of 5760 x 4092 TEM images at 37.5 frames per second at 1.9 Å pixel size, and a low electron dose rate of just 2.1 $e^-/Å^2/s$, which is several orders of magnitude less than a typical high-resolution TEM image.

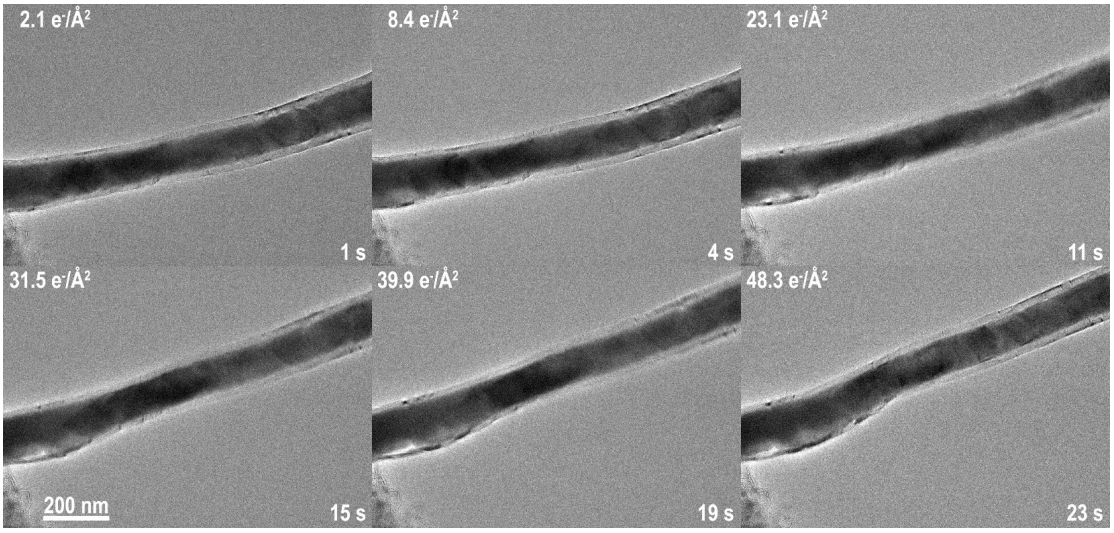

Figure 1. *In-situ* imaging. Lithiation progressed under -6 V of potential, where the Li-ions traveled down the inner wall of the CNT and alloyed with the NiS. Lithiation progressed from the perimeter of the Ni_3S_2 into the core, where the lithiation front progressed quickly down the CNT inner walls. As the Ni_3S_2 alloyed with lithium, the volume expansion caused strain on the CNT enclosure, which eventually caused the fracture of the CNT. Each frame displayed here represents 40 original frames that were summed, leading to minor blurring not present in the raw data due to sample rotation. The dose displayed is the cumulative dose since the start of this video.

Summary

The dynamic changes in the lithiation events identified that the rate of lithiation caused enormous strain to the walls of the CNT, which resulted in a fracture. The lithiation front was observed to move fastest along the CNT interface with the Ni_3S_2 filler. These images are contrary to the expected mechanism for Ni_3S_2 volume expansion during lithiation, being that volume expansion would be confined to the transverse direction of the CNT. The K3 IS was able to capture this fast reaction at a high temporal and spatial resolution without interfering with the beam sensitive lithiated materials.

Credit(s)

A special thanks to the Center for Integrated Nanotechnologies (CINT) and Katherine L. Jungjohann. The materials were synthesized by Dr. Wenzhi Li's research group in the Department of Physics at Florida International University.

Gatan, Inc. is the world's leading manufacturer of instrumentation and software used to enhance and extend electron microscopes—from specimen preparation and manipulation to imaging and analysis.

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