

A NANOCOMPOSITE ANODE FOR BETTER BATTERIES?

One of the most promising pathways to the goal of more efficient rechargeable lithium-ion (Li-ion) battery technology is finding and developing new materials with better capacity and cycling performance. Anode materials such as tin phosphide (Sn_4P_3) have demonstrated far greater performance capacity than conventional graphite anodes but also a high fading rate. Researchers from the Illinois Institute of Technology and Ohio University have developed a novel nanocomposite anode combining the high capacity of Sn_4P_3 and the high electrical conductivity of graphite. Employing APS high-brightness x-ray beams, they performed *in situ* extended x-ray absorption fine structure (EXAFS) studies of the new composite, showing the resulting local structural changes in an operating cell and allowing detailed modeling of the lithiation/delithiation mechanism. The composite demonstrated a reversible capacity of 651 mA h g^{-1} after 100 cycles, unlike pure Sn_4P_3 anode, which rapidly fades after about 20 cycles.

Previous attempts to study Sn_4P_3 using x-ray diffraction (XRD) showed that its crystal structure was quickly lost with lithiation, becoming amorphous and rendering further XRD measurements essentially useless. Other *ex situ* studies of Sn_4P_3 electrodes using x-ray absorption fine structure (XAFS) and XRD revealed an apparently irreversible conversion reaction after several cycles. The present work sought an understanding of the highly reversible lithiation/delithiation mechanism observed in the new composite anode material through *in situ* EXAFS, performed at the MR-CAT 10-ID-B beamline at the APS.

Initial XRD characterization of the synthesized Sn_4P_3 /graphite composite showed peaks matching the usual Sn_4P_3 crystalline structure. The EXAFS analysis takes into account some difficulties inherent in examining operating coin cells, particularly the need for faster cycling in order to reproduce a number of repeated full cycles in the limited time available under experimental conditions. To overcome this, the researchers used the data from the first four cycles for their analysis and modeling and included the measurements from an *ex situ* electrode sample after 100 cycles. They observed that after the first two cycles, an amorphous SnP_x phase develops, completely

replacing the crystalline Sn_4P_3 . This amorphous phase structure contributes to highly reversible conversion and alloying processes in subsequent cycles, with amorphous SnP_x initially converting to metallic Sn clusters and Li_3P , followed by alloying of metallic Sn with Li-ions.

This amorphous SnP_x phase is the main reason for the marked superiority in reversibility and capacity in the

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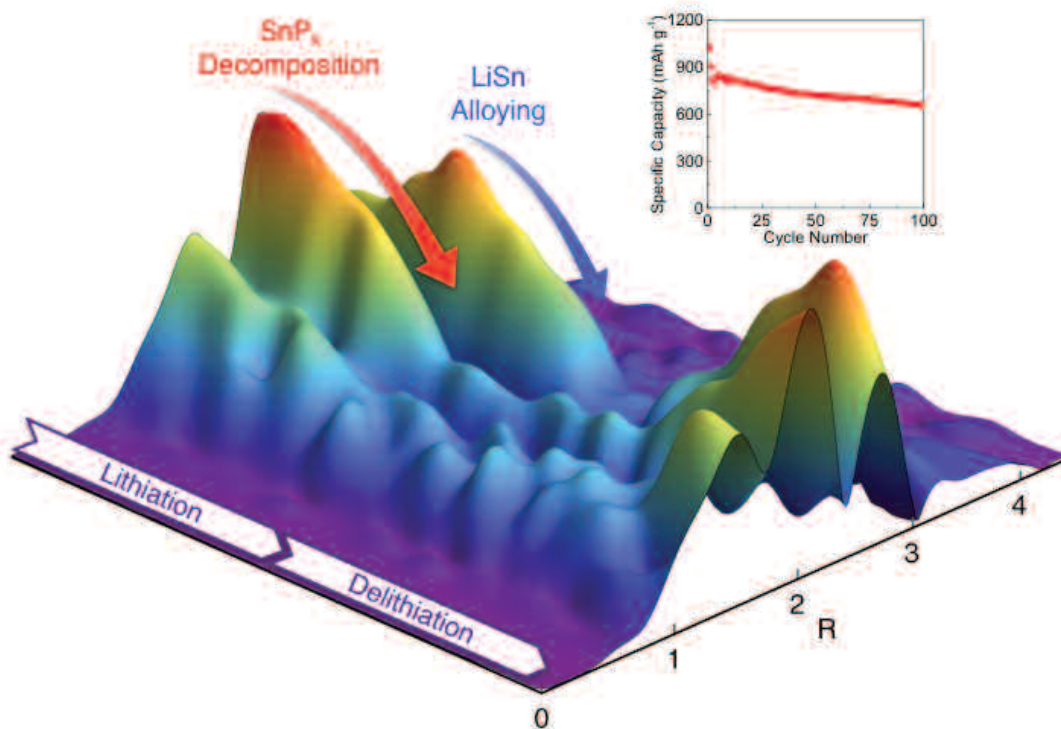


Fig 1. Three-dimensional surface plot of $|\chi(R)|$ as a function of cell capacity for the entire third *in situ* cycle of the Sn_4P_3 /graphite composite anode. The initial loss of the SnP_x phase (red arrow) is followed by growth and then loss of Sn metal clusters (blue arrow) as full lithiation is achieved. The inset shows the 100-cycle capacity of a Sn_4P_3 /graphite composite coin cell charged at a rate of 100 mA g^{-1} .

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Sn₄P₃/graphite composite material compared with pure crystalline Sn₄P₃. The experimenters propose that this is best explained by the presence of the graphite matrix forming after high-energy ball milling, which allows electrical conductivity among the widely dispersed SnP_x clusters throughout the material. The graphite matrix also prevents aggregation of Sn clusters during lithiation/delithiation, thus preserving greater capacity for longer periods. The researchers attribute the eventual capacity fading to the slow increase in metallic Sn-Sn cluster sizes observed with EXAFS over cycling.

The detailed picture of the conversion and alloying mechanisms at work in these tin phosphide anode materials seems to indicate that the use of graphite provides one possibility for enhancing their capacity and cycle life. Use of the *in situ* XAFS technique enables detailed understanding of factors affecting reversibility of redox processes in battery materials, which will be instrumental for further performance improvement. — *Mark Wolverton*

See: Yujia Ding¹, Zhe-Fei Li², Elena V. Timofeeva¹, and Carlo U. Segre^{1*}, “In Situ EXAFS-Derived Mechanism of Highly Reversible Tin Phosphide/Graphite Composite Anode for Li-Ion Batteries,” *Adv. Energy Mater.* **8**, 1702134 (2018,).

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.8-32 keV, 15-65 keV • On-site • Accepting general users •