In Situ EXAFS Study of Tin Phosphide/Graphite Composite Anodes for Lithium-Ion Batteries

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A promising conversion-type anode material for LIB.
Sn₄P₃: 9Li₁⁺ + 9e⁻ ↔ 4Sn + 3Li₃P; Sn + 4Li₁⁺ + 4e⁻ ↔ Li₄Sn.

Advantages:
• High theoretical capacity: 1255 mAh/g;
• High volumetric density;
• Low cost;

Challenges:
• More than 200% volume change during charge/discharge;
• Phase segregation during lithiation

Synthesis

EXAFS data was collected at the Sn K-edge in fluorescence; Measurements were taken from a kapton window on the in situ coin cell, during the cell is operating:
• The origin represent the center Sn atoms. The peaks represent paths between center Sn atoms and their near neighbors.

EXAFS as a function of capacity shows the process of lithiation and delithiation of 3rd cycle.

![EXAFS](image)

Advantages:
• Does not depend on long range crystalline order;
• A powerful technique to study mechanism of lithiation and delithiation process in situ.

Analysis Steps:
• Remove background
• Apply k-weighting
• Fourier transform into R space
• Fit with a structural model
• Extract local structural parameters: Number of near neighbors and atomic distance.

Electrochemistry

Sn₄P₃/Graphite anodes exhibit excellent electrochemical performance compared to pure Sn₄P₃.

Possible Explanation:
Sn₄P₃ is uniformly distributed within graphite matrix. During the discharge process, the formed LiP and Li₄Sn phases are tightly confined in the conductive graphite matrix.

Add 10% FEC into electrolyte
• Form a stable SEI layer;
• Improve cycle life and coulombic efficiency.

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Study the mechanism of improved performance of Sn₄P₃/Graphite by in situ EXAFS

X-ray absorption fine structure Fundamentals
An atom absorbing an X-ray with the resultant ejection of a core electron into the continuum.

XANES and EXAFS:
X-ray absorption near edge structure and extended X-ray absorption fine structure

Interference patterns created by the ejected photoelectron expands as a spherical wave, reaches the neighboring electron clouds, and scatters back to the core hole.

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![EXAFS](image)

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![EXAFS](image)

In Sn₄P₃/Graphite, no P near neighbors left in charge data and no Li near neighbors left in discharge data. In contrast, Sn-P and Sn-Li exists in both charge and discharge data of pure Sn₄P₃.

These results demonstrate Sn₄P₃/Graphite has much better reversibility than pure Sn₄P₃.