**In Situ EXAFS-Derived Mechanism of Highly Reversible Tin Phosphide/Graphite Composite Anode for Li-Ion Batteries**

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### Synthesis and Electrochemistry of Sn₄P₃/Graphite

Sn₄P₃ is a promising conversion-type anode material for LIB with a theoretical capacity of 1255 mAh/g.

- **Red phosphorus**
- **Molar ratio: 4:3**

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### In Situ EXAFS Experiment

EXAFS data were collected at the Sn K-edge (29.2 keV) in fluorescence mode while the in situ coin cell was cycled galvanostatically, at MRCAT APS Sector 10-ID beamline.

- XRD patterns of as-synthesized Sn₄P₃/graphite composite
- All the peaks match the Sn₄P₃ crystal structure, except the "***" peak from the mounting clay in the sample holder

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### Mechanism of Improved Cycling Performance

#### [X(R)] plots of Sn₄P₃/graphite at OCV (black), lithiated (blue), and delithiated (red) states in the 3rd cycle

**Black:** Crystal structure of Sn₄P₃; High Sn-O peak is from particle surfaces or an amorphous oxide phase; **Red:** Three high intensity peaks from amorphous phase; Never returns to the original crystal structure; **Blue:** Low intensity peaks from LiSn alloys.

- Minor changes between the 3rd lithiated and delithiated states
- No amorphous Sn₄P₃ phase formed in pure Sn₄P₃

#### Dynamic snapshot of [X(R)] in the entire 3rd cycle

- Amorphous Sn₄P₃ phase and small metallic Sn clusters is reversibly formed in the delithiated states after the 2nd cycle, and completely decomposed in the later lithiated states. The Sn₄P₃ phase possibly exist in a tetrahedral configuration that contains only first shell P neighbors.
- The 3rd and 4th lithiated states show a mixed environment with LiSn alloys and remaining metallic Sn clusters. All Li atoms are extracted from the alloys in delithiated states.
- The gradual capacity loss after 100 cycles is due to reduced Sn₄P₃ phase and larger Sn clusters after long-term cycling.

#### Capacities comparison between in situ coin cell (black) and regular coin cell (red)

- In situ capacities reached about 80% of the regular cell in the 3rd cycle;
- Low in situ capacities are due to lower pressure and poor electrical contact in the Kapton window used for data collection.

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### In Situ EXAFS-Derived Mechanism of High Reversibility Tin Phosphide/Graphite

The Sn₄P₃/graphite composite (red) exhibits excellent electrochemical performance compared to pure Sn₄P₃ (blue), with a reversible capacity of 651 mAh/g in the 100th cycle.

- Sn₄P₃ Electrodes: 50% active materials, 10% CMC binder, 40% SuperP
- Sn₄P₃/Graphite Electrodes: 80% active materials, 10% CMC binder, 10% SuperP
- Electrolytes: 1.2 M LiPF₆ in EC/DMC 3:7 with 0.2% FEC

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