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

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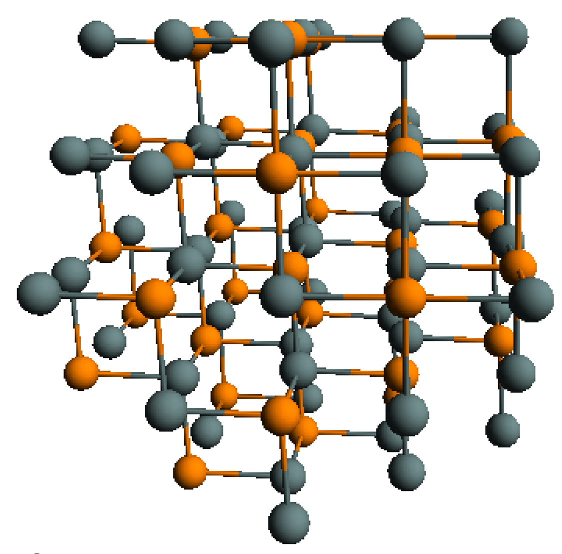
Sn_4P_3

A promising conversion-type anode material for LIB.

$Sn_4P_3 + 9Li^+ + 9e^- \longleftrightarrow 4Sn + 3Li_3P$;

$Sn + 4.4Li^+ + 4.4e^- \longleftrightarrow Li_{4.4}Sn$.



Advantages:

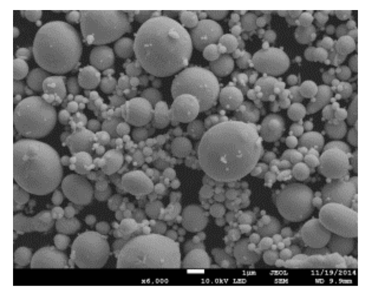
- High theoretical capacity: 1255 mAh/g;
- High volumetric density;
- Low cost;

Challenges:

- More than 200% volume change during charge/discharge;
- Phase segregation during lithiation

Synthesis

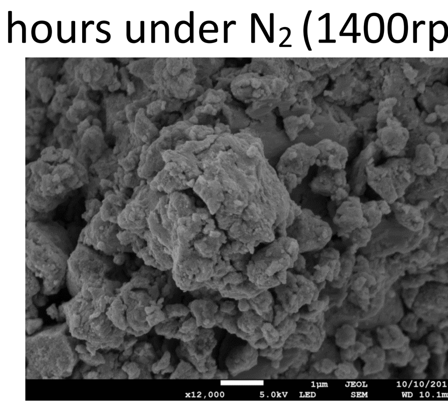
Sn



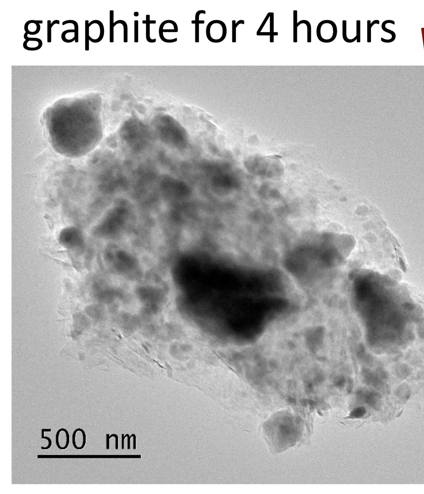
Red phosphorus

Molar ratio 4:3

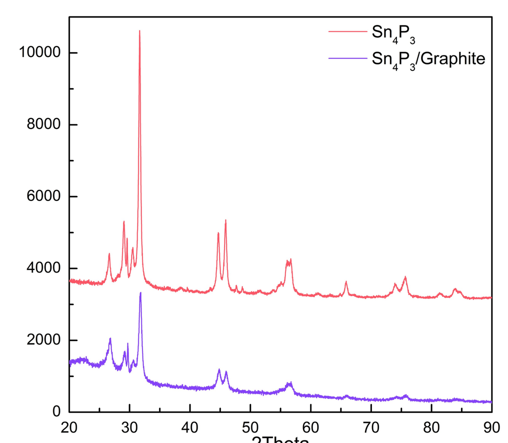
High energy ball milling for 6 hours under N_2 (1400rpm)



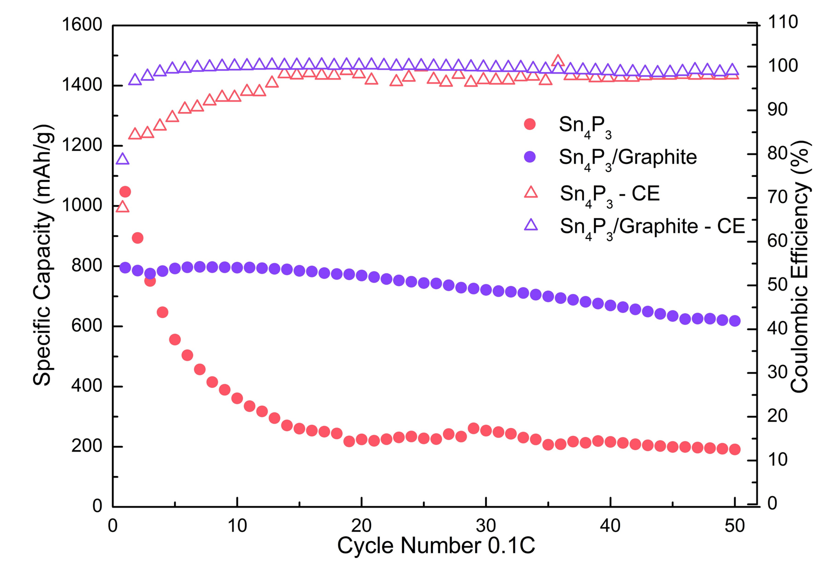
Ball milling Sn_4P_3 and graphite for 4 hours



Weight ratio 7:3



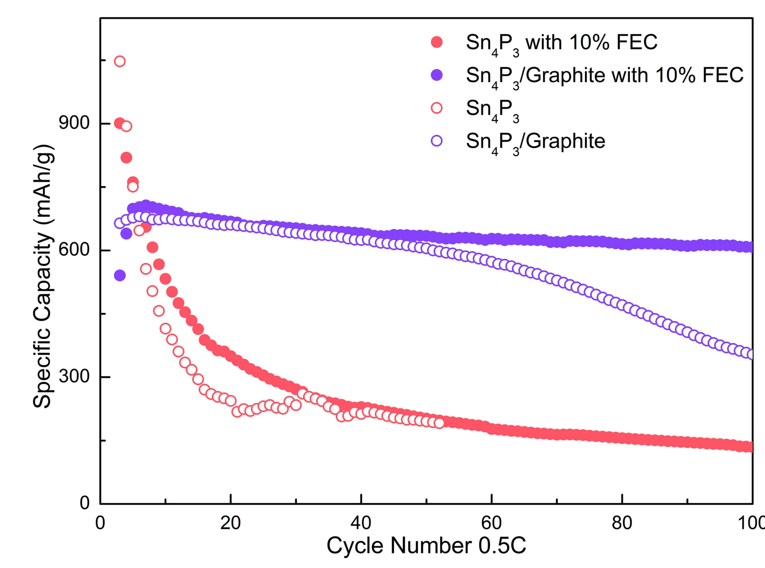
Electrochemistry



Electrodes composition

Sn_4P_3: 50% active materials, 10% CMC binder, 40% SuperP

Sn_4P_3/Graphite: 80% active materials, 10% CMC binder, 10% SuperP



Electrolyte:

1.2 M $LiPF_6$ in EC/EMC 3:7 with/without 10% FEC

Sn_4P_3/Graphite anodes exhibit excellent electrochemical performance compared to pure Sn_4P_3

Possible Explanation:

Sn_4P_3 is uniformed distributed within graphite matrix. During the discharge process, the formed Li_3P and Li_xSn phases are tightly confined in the conductive graphite matrix.

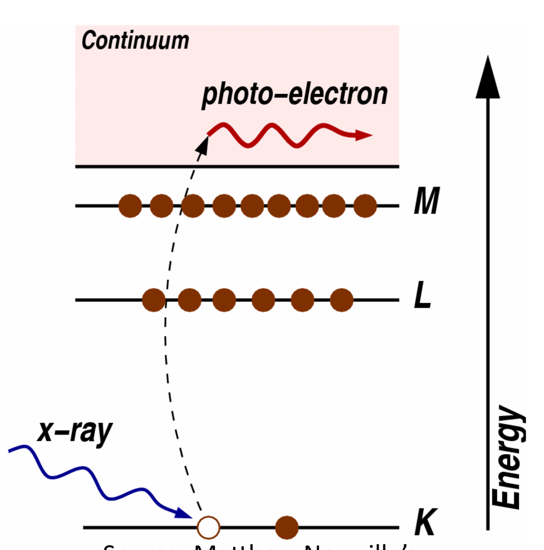
Add 10% FEC into electrolyte

- Form a stable SEI layer;
- Improve cycle life and coulombic efficiency.

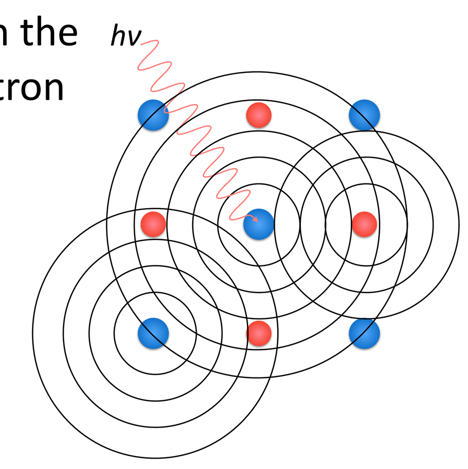
Study the mechanism of improved performance of Sn_4P_3/Graphite by in situ EXAFS

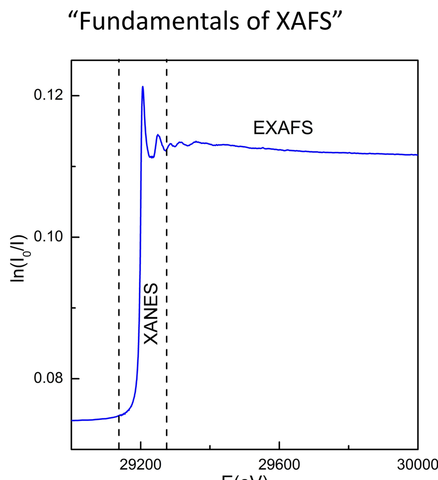
X-ray absorption fine structure Fundamentals

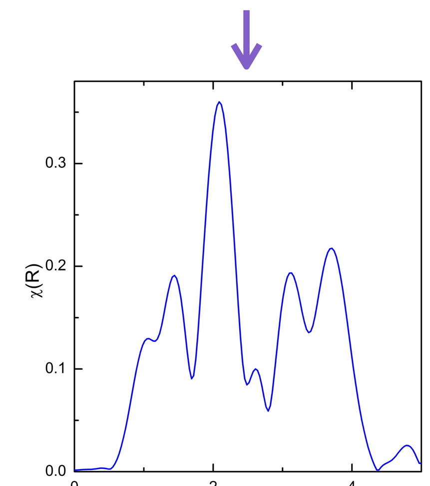
An atom absorbing an X-ray with the resultant ejection of a core electron into the continuum.



Sourse: Matthew Newville's "Fundamentals of XAFS"







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.

Analysis Steps:

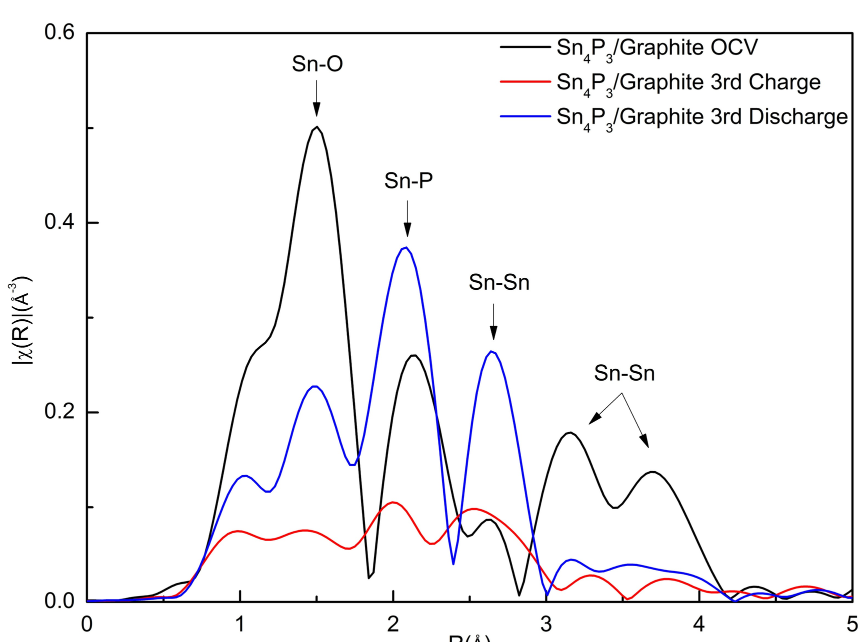
- Remove background
- Apply k-weighting
- Fourier transform into R space
- Fit with a structural model
- Extract local structural parameters: Number of near neighbors and atomic distance.

Advantages:

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

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.

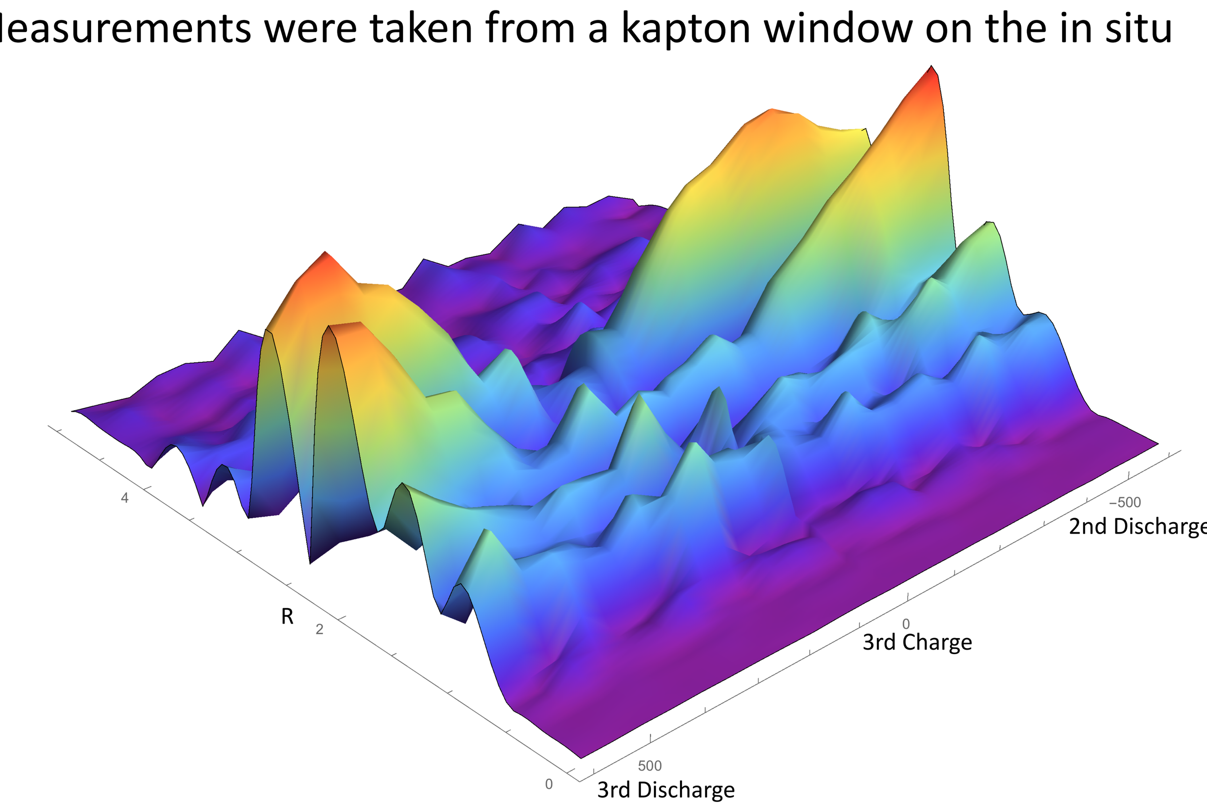


Black: crystal structure of Sn_4P_3, and higher Sn-O generated by ball milling.

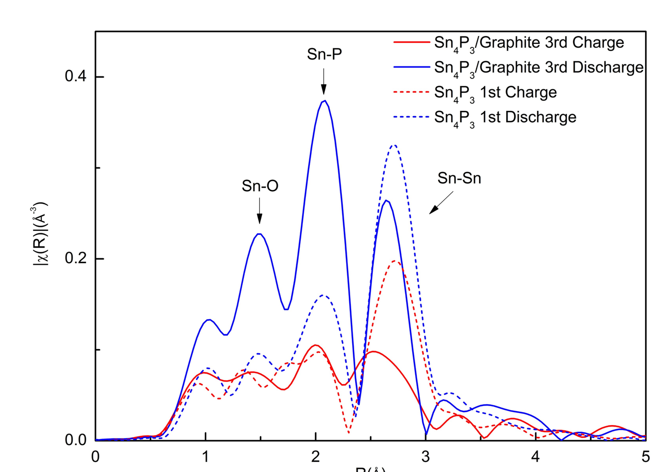
Red: converted to Li_xSn alloy, and no Sn-P path left.

Blue: Sn-P and Sn-Sn paths reappear, and no Li left.

Tin phosphide is generated in a different amorphous structure rather than the original crystal structure.

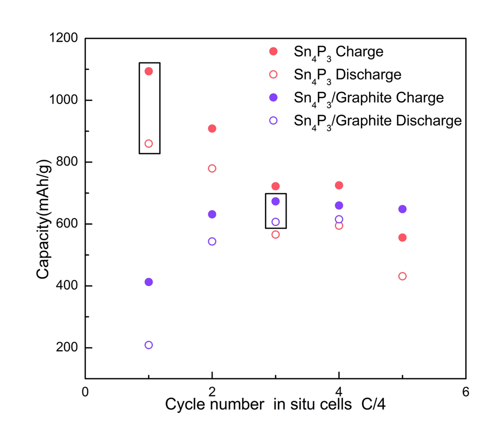


EXAFS as a function of capacity shows the process of lithiation and delithiation of 3rd cycle.



Dashed curves:

slight changes in all paths.



	Near Neighbors			
Paths	Sn-O	Sn-P	Sn-Sn	Sn-Li
Sn_4P_3/Graphite 3rd Charge	0.3 ± 0.1		1.5 ± 0.2	7.6 ± 0.7
Sn_4P_3/Graphite 3rd Discharge	0.8 ± 0.2	1.4 ± 0.2	1.3 ± 0.3	
Sn_4P_3 1st Charge	0.3 ± 0.1	0.5 ± 0.1	1.9 ± 0.3	4.4 ± 0.5
Sn_4P_3 1st Discharge	0.3 ± 0.1	0.5 ± 0.2	2.3 ± 0.3	2.6 ± 0.7

In Sn_4P_3/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 Sn_4P_3.

These results demonstrate Sn_4P_3/Graphite has much better reversibility than pure Sn_4P_3.

- Select 3rd cycle of Sn_4P_3/Graphite and 1st cycle of Sn_4P_3 as representatives. Because these cycles have the highest capacities and have the most lithiated data and the most delithiated data.
- Performance of in situ cells are not as good as normal coin cells. The sample in the window area may show worse reversibility than the rest of cell, because of the lower pressure.

Acknowledgement:

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