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Insitu Analysis of $LiFePO_4$ Batteries: Signal Extraction by Multivariate Analysis

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Motivation

- We would like to understand the inner workings of a $LiFePO_4$ based Li-ion battery during charge/discharge (i.e. work cycle).
  - Correlate electrochemical and structural changes in battery

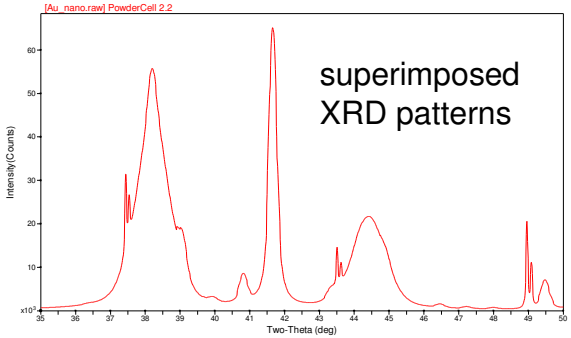
Approach

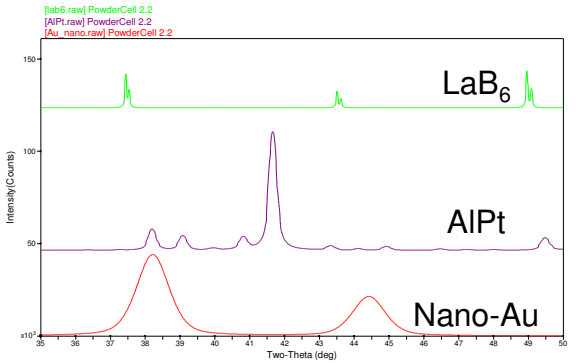
- Use neutron diffraction to monitor battery insitu (during cycling).
  - Benefits of neutron diffraction:
    - Highly penetrating beam & ***Li sensitivity***
    - No need for modification of existing cell design (from shelf to beam).
- Employ Principle Component Analysis (PCA) to decompose convoluted datasets from measurement.

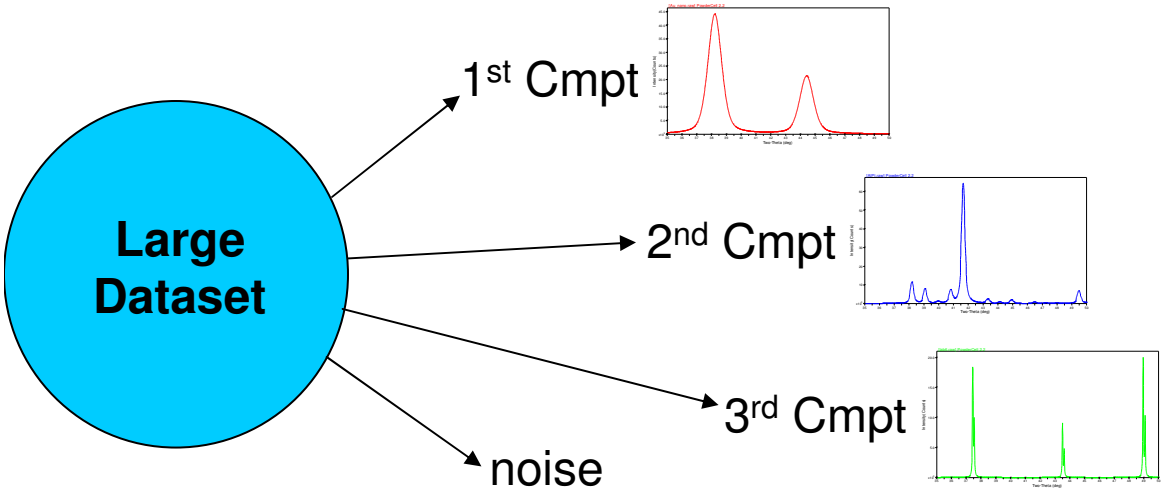
Question: What is Principal Component Analysis (PCA)?

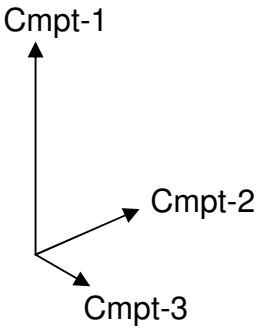
Answer: A common form of Multivariate Analysis (MVA) we use to analyze large datasets.

We assume that the entire dataset can be represented by linear combinations of all the diffracting species









Each derived component is mathematically constrained* to be orthogonal to others

*Note: This constraint is physically meaningless. Oftentimes one has to modify PCA to improve the physical assignment of components.

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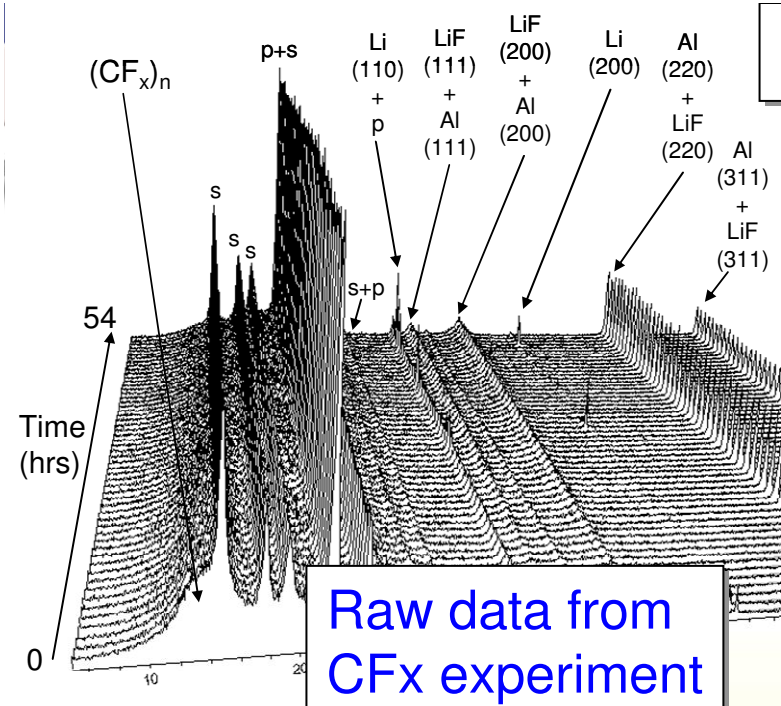
Past success using XRD insitu data



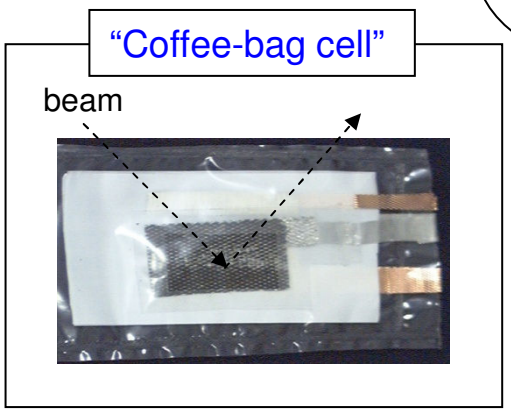
Insitu datasets are convoluted with signal from entire specimen. ☹

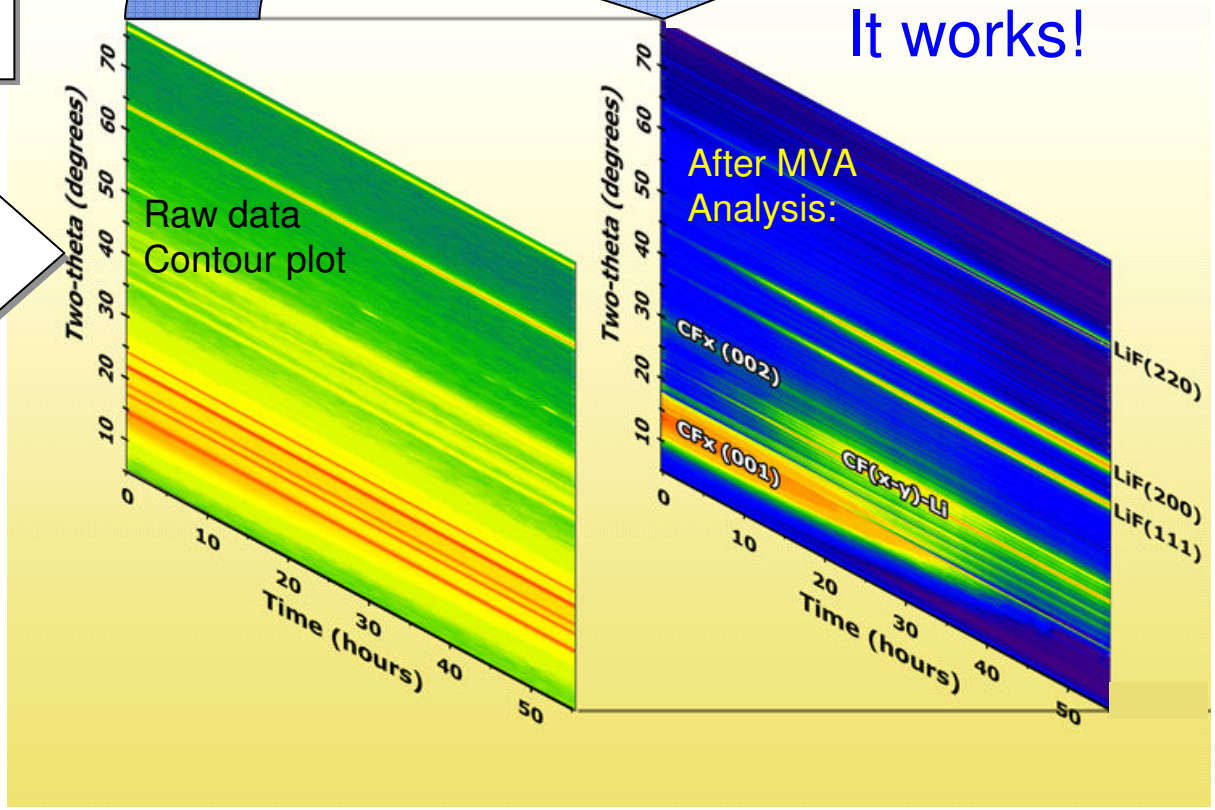
We employed Principle Component Analysis (PCA) to obtain Rx behavior of insitu battery from XRD data. ☺

Raw data from CFx experiment

PCA

It works!





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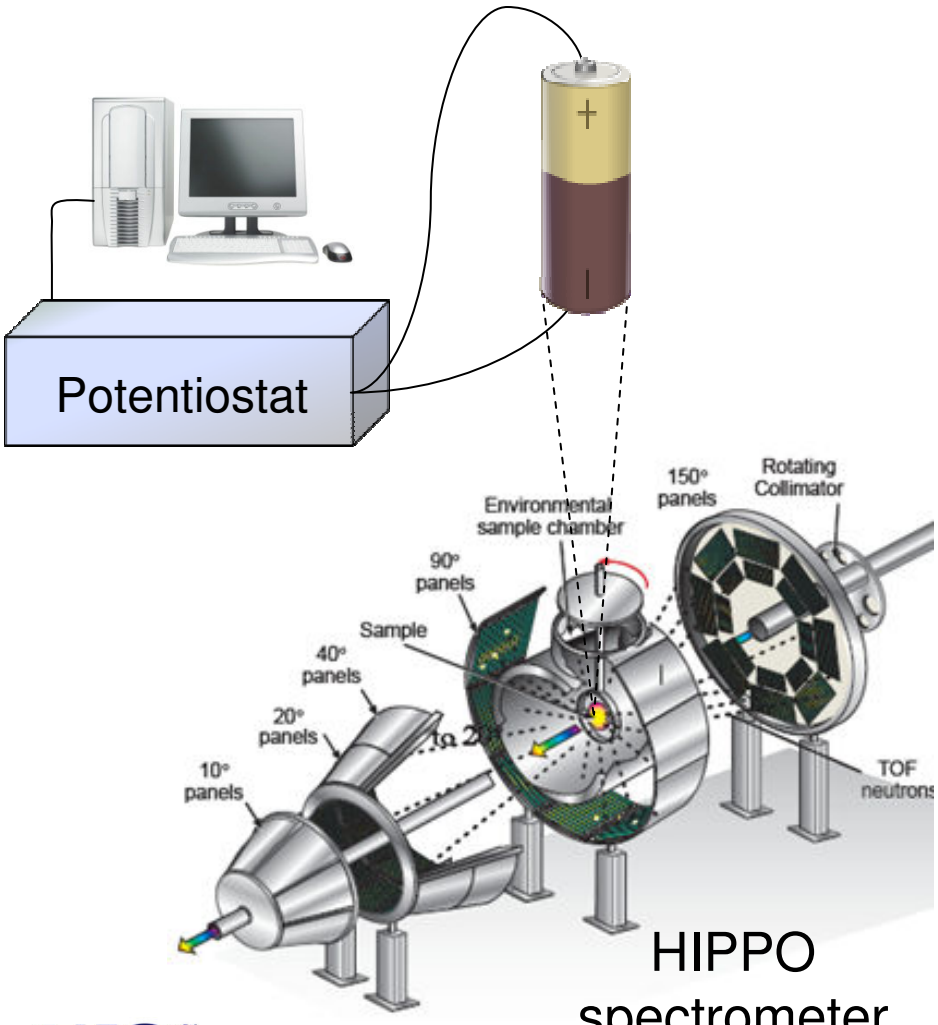
Can we do the same type of experiment with neutrons?



HIPPO spectrometer

Experimental setup

- A commercial $LiFePO_4$ battery was electroded and placed in the HIPPO spectrometer at LANSCE, LANL
- Experiment began with cell at 100% State-of-Charge (SOC).
- Cell was set to a given SOC via potentiostat (~1/2 hr to remove 10% of Li)
- Sample was held at given SOC for ~1hr while TOF neutron diffraction data were collected.
- Cell was discharged, recharged and discharged again over 24hr period.

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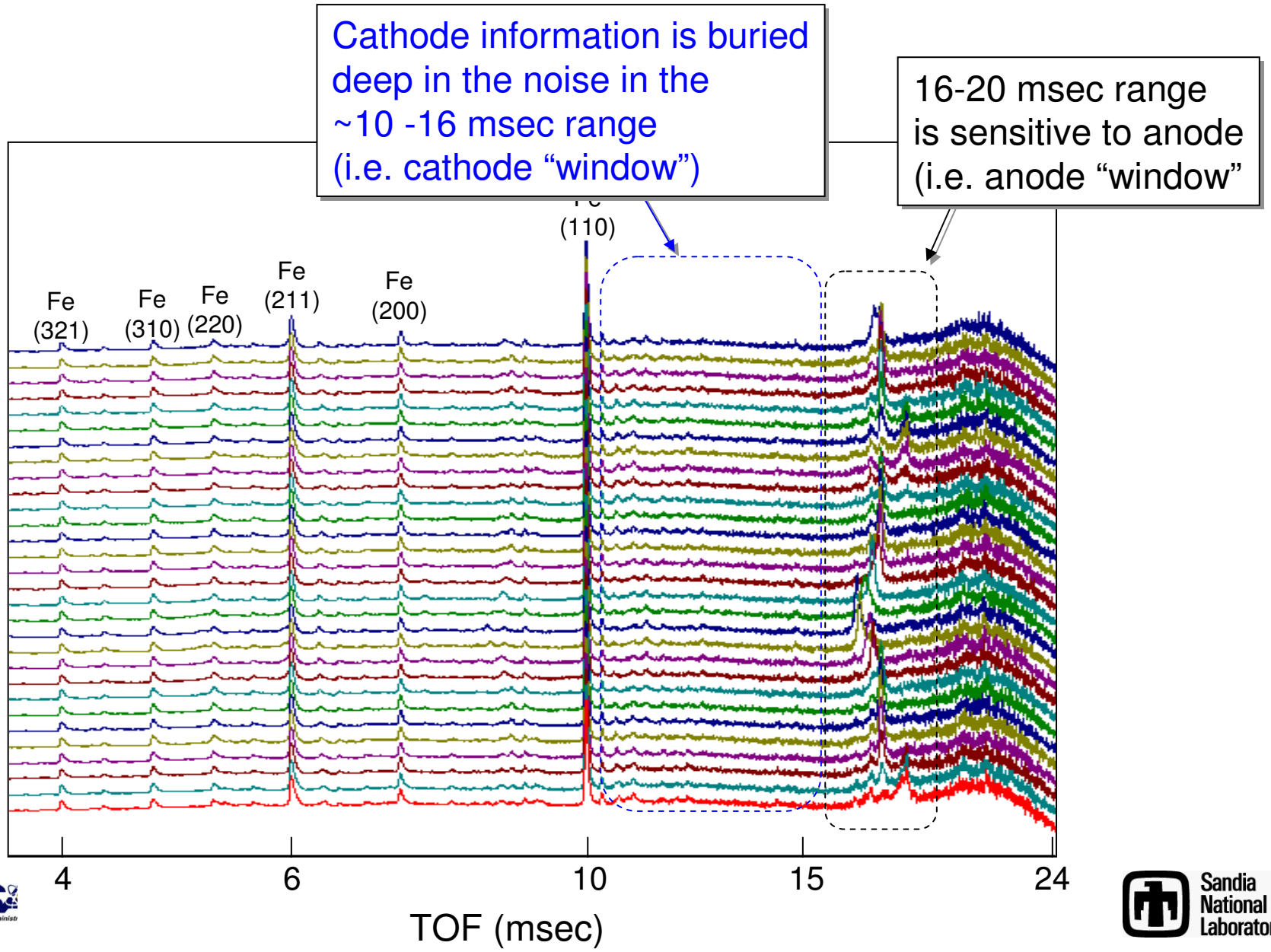
Changes in anode were immediately observed in neutron diffraction raw data. It was hard to see changes in cathode peaks (low intensity).



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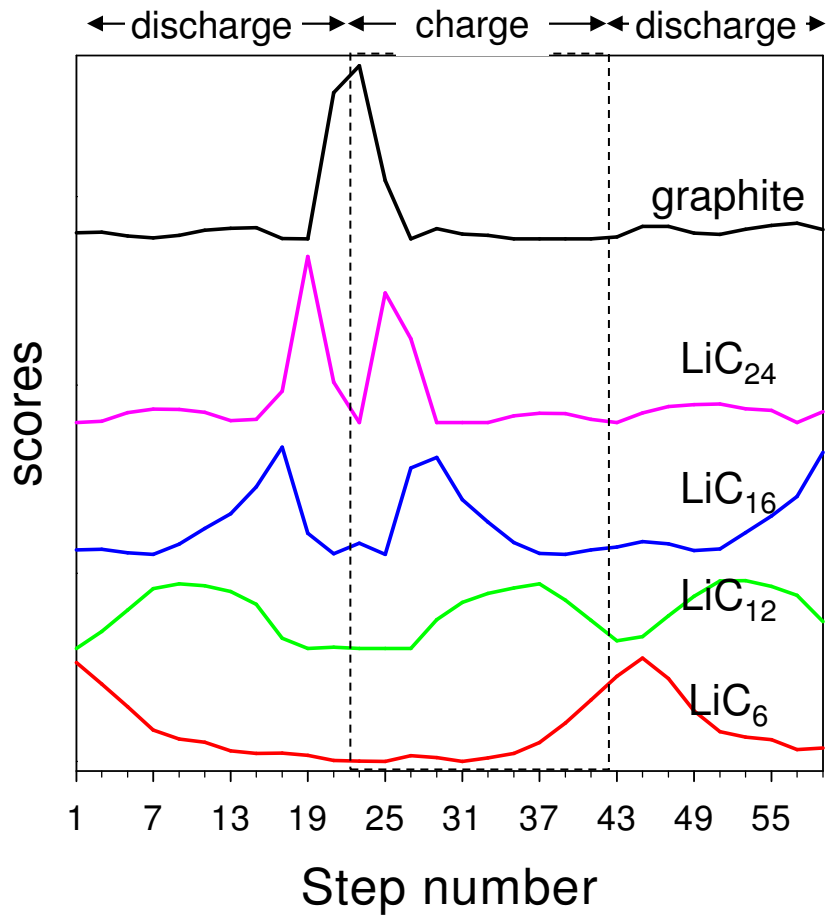
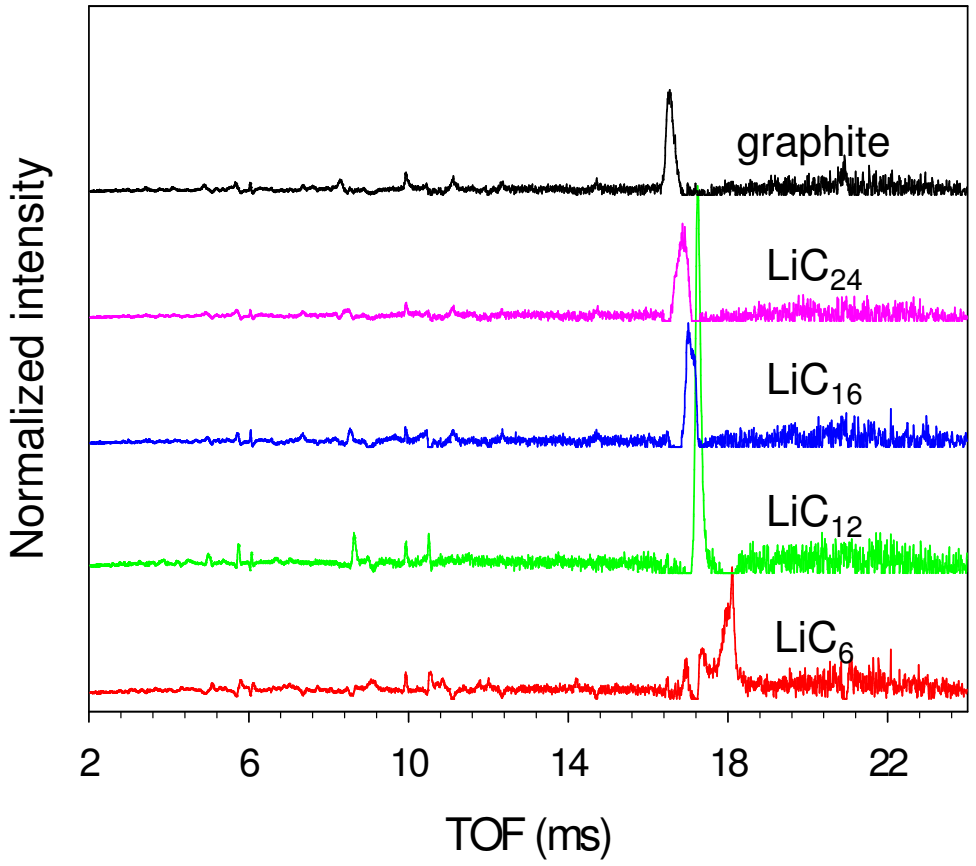
- 1st PCA attempt with full histograms (150° banks) yielded a six component system composed of:
  - Inert component representing average pattern
  - 5 components which can be assigned to various stagings of LiC_x





Anode staging tracks well with battery cycling

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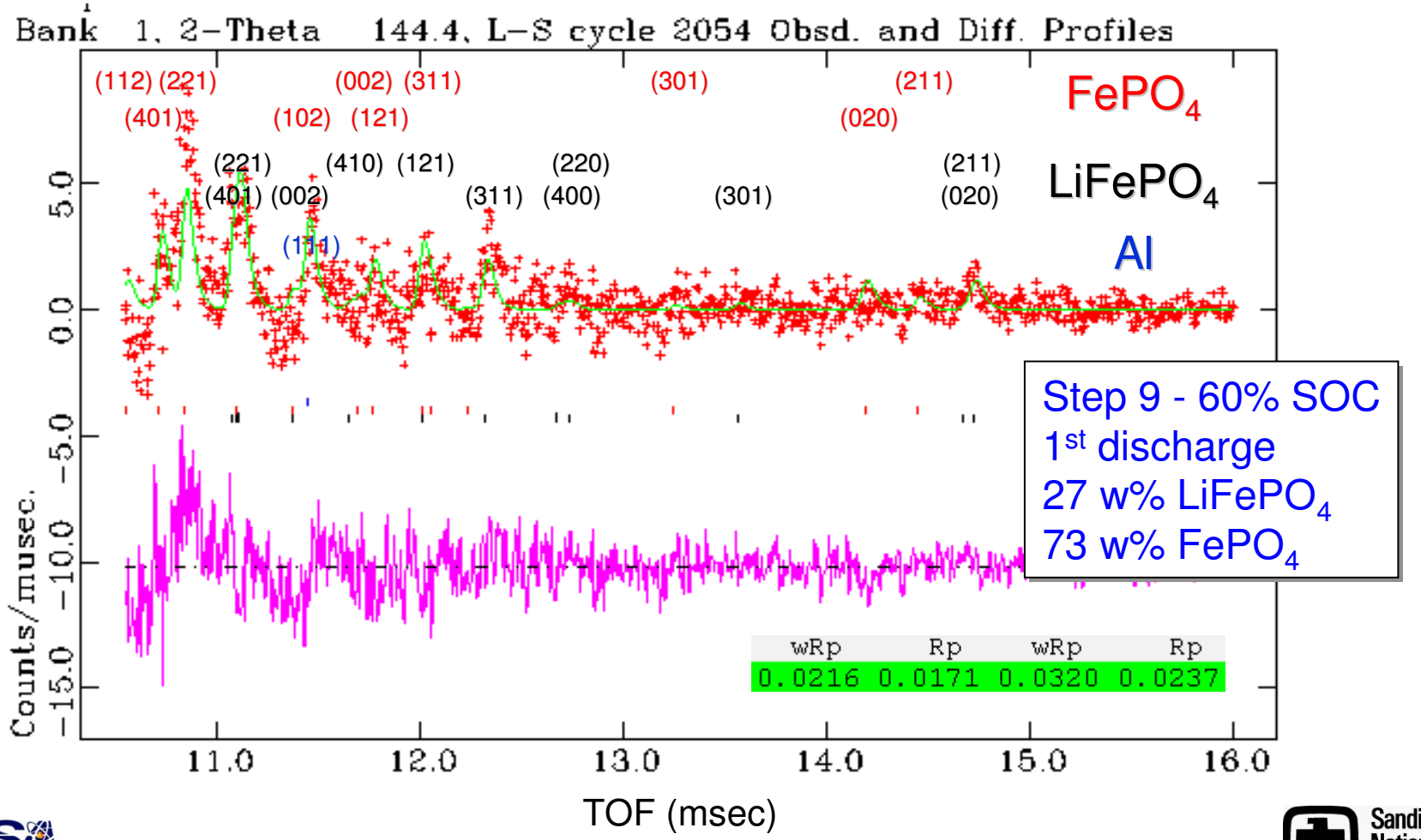
- Datasets are very noisy for cathode TOF window of analysis.
- Fortunately $LiFePO_4$ and $FePO_4$ do not vary much with cycling.
  - We can fix lattice parameters, atom positions*

A.S. Andersson, et. al
Solid state Ionics
130 41-52 (2000).

- Individual refinements monitor $LiFePO_4/FePO_4$ phase fraction



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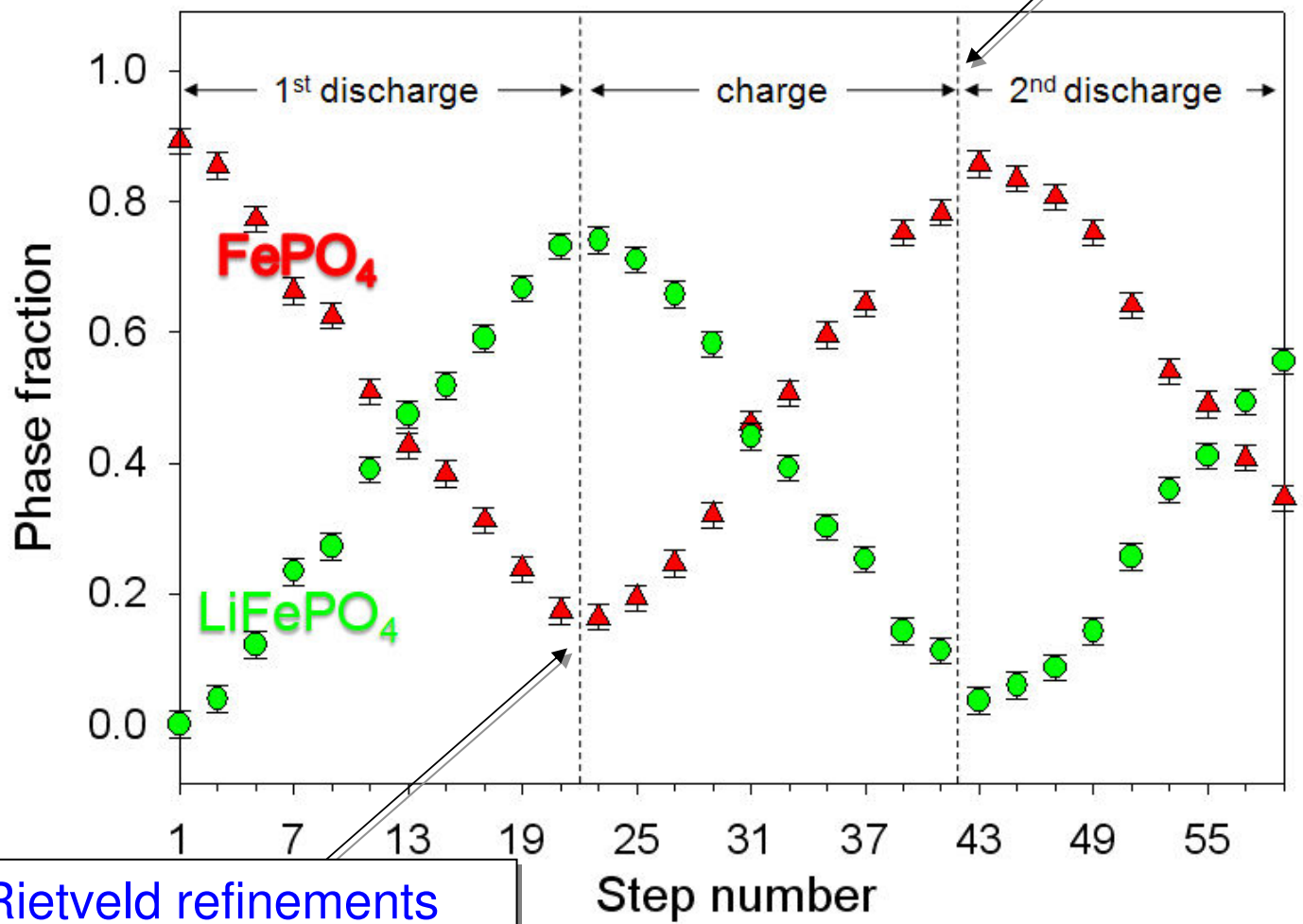
Phase fraction results from Rietveld structure refinements

Note that there is a delayed response of cathode when switching to 2nd discharge cycle



Rietveld refinements indicate ~15 w% $FePO_4$ remains at 0 SOC.

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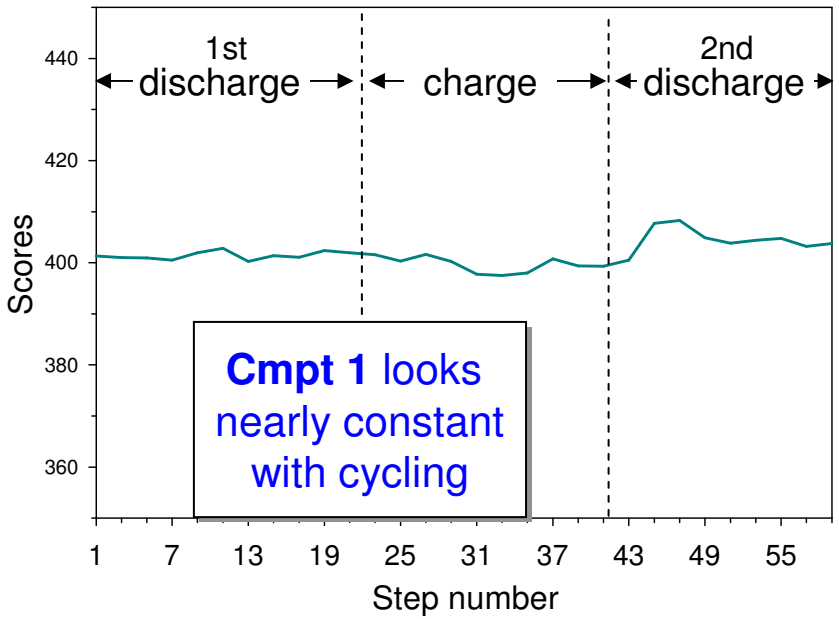
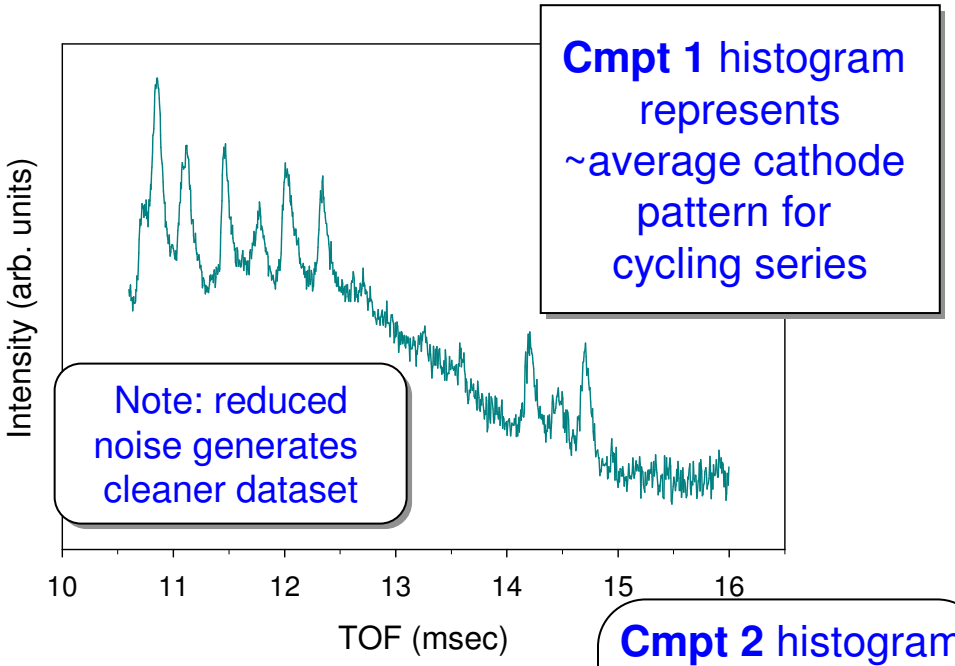
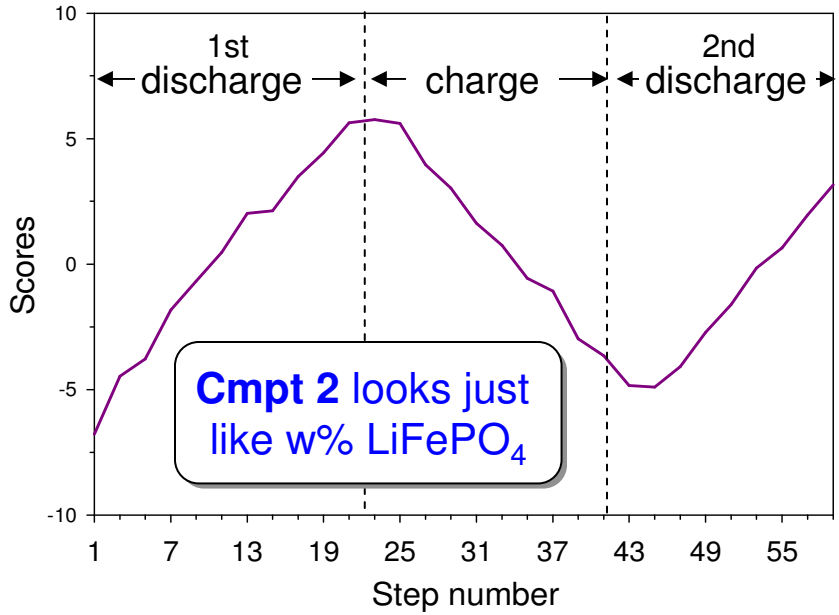
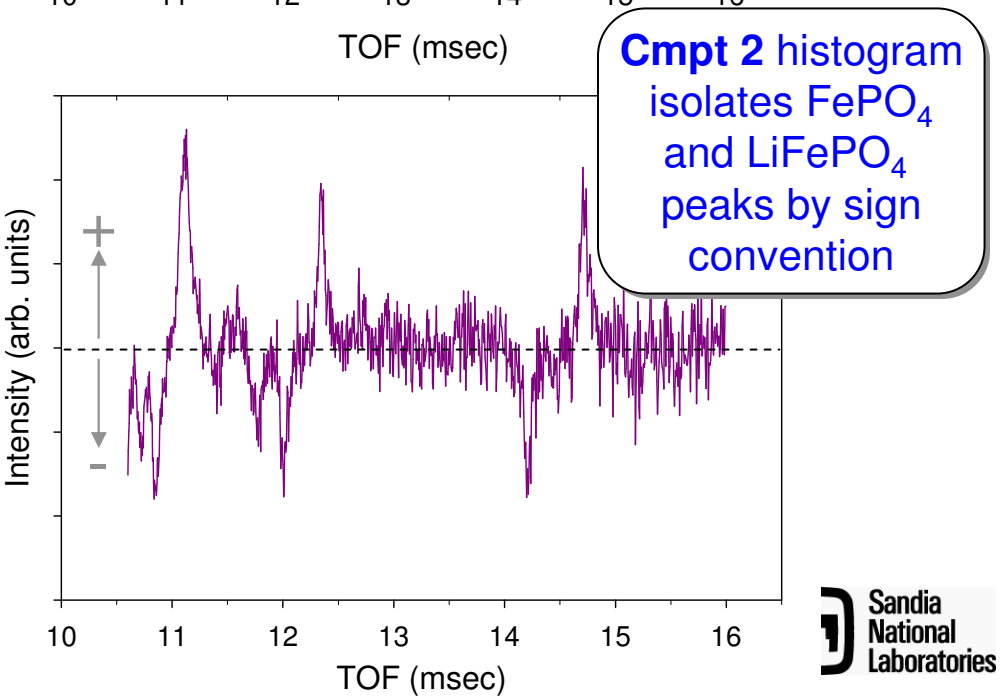
- PCA on cathode TOF window yields a simple 2 component system.









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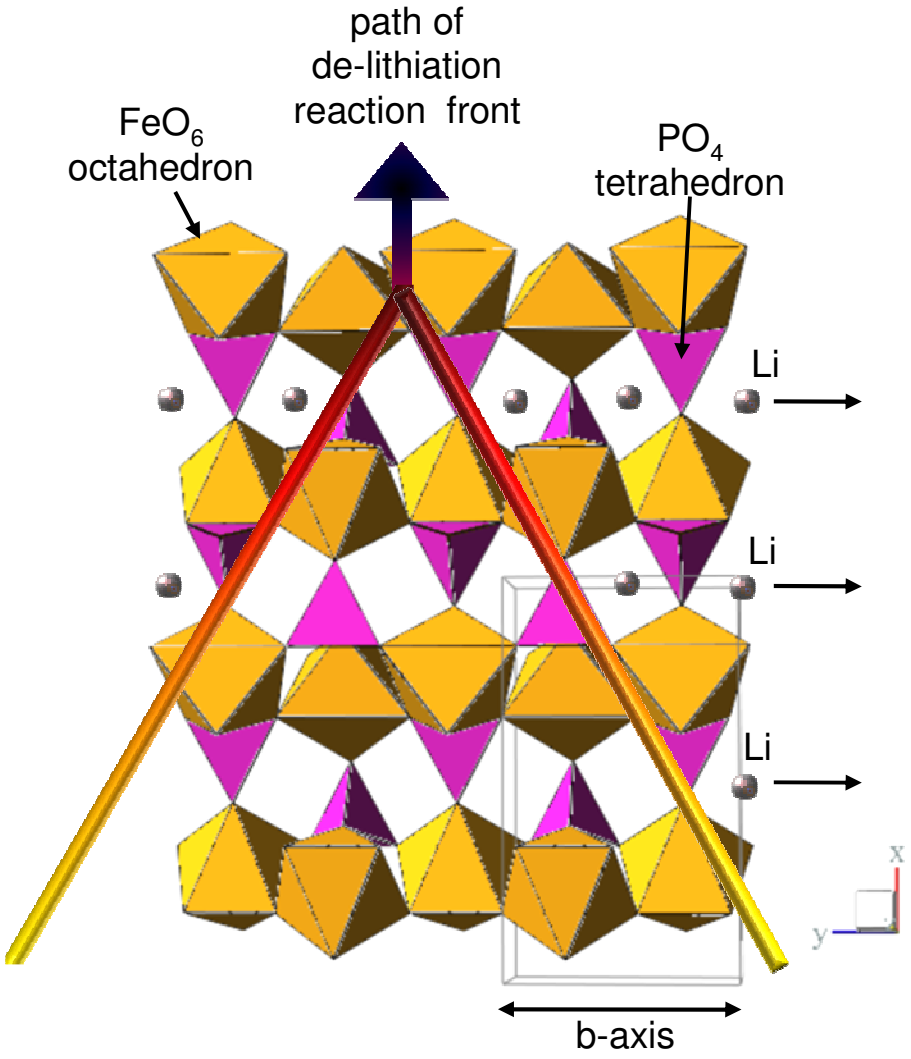
Interfacial transport theory of Li in $LiFePO_4$ cathodes



- Laffont, et. al* has suggested that Li transport occurs by "unzipping" the Triphylite $LiFePO_4$ phase.
- Li atoms are thought to propagate out of the host lattice via the b-axis, leaving behind the Heterosite $FePO_4$ compound
- Intercalation of Li occurs in the reverse fashion.

*L. Laffont, et. al, *Chem. Mater.,* **18** 5520-5529 (2006).

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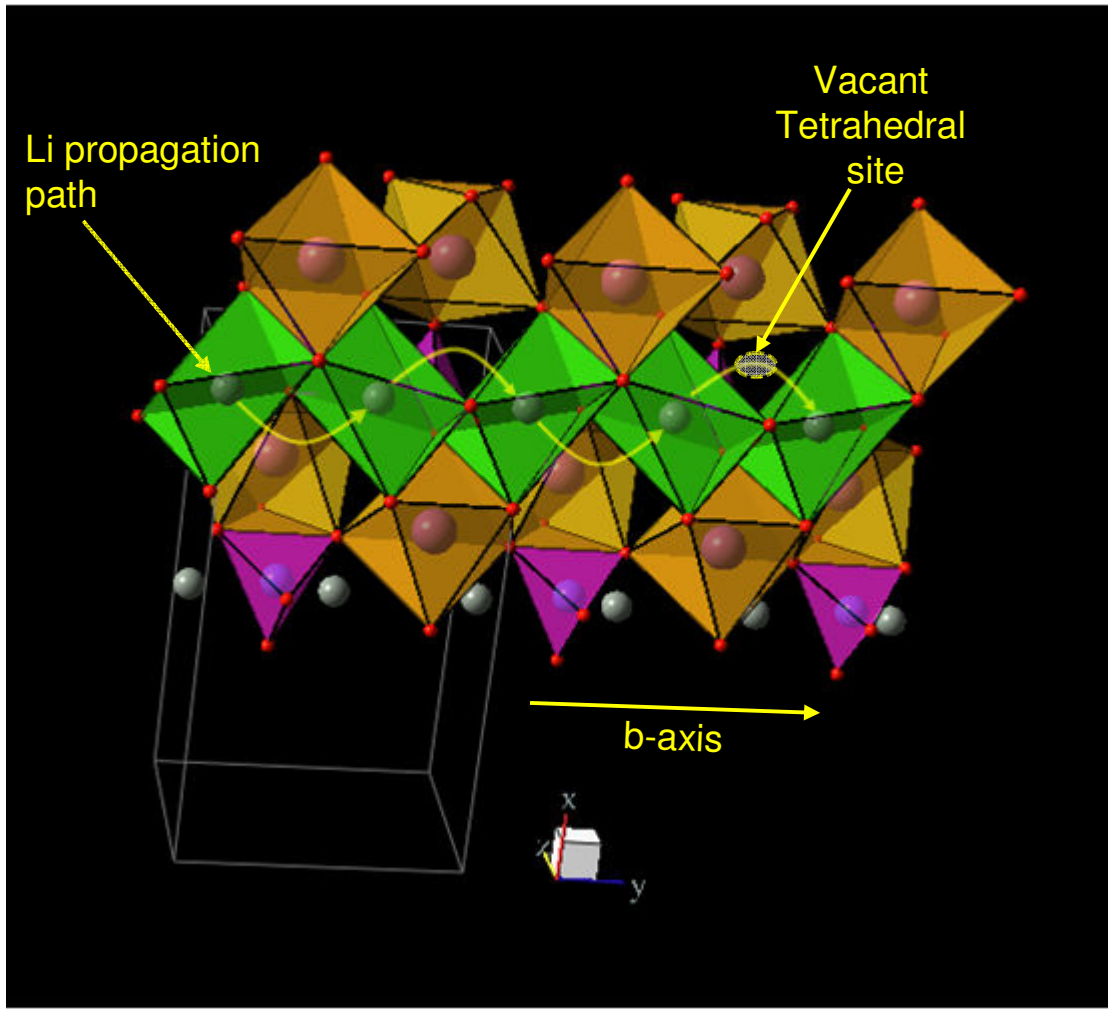
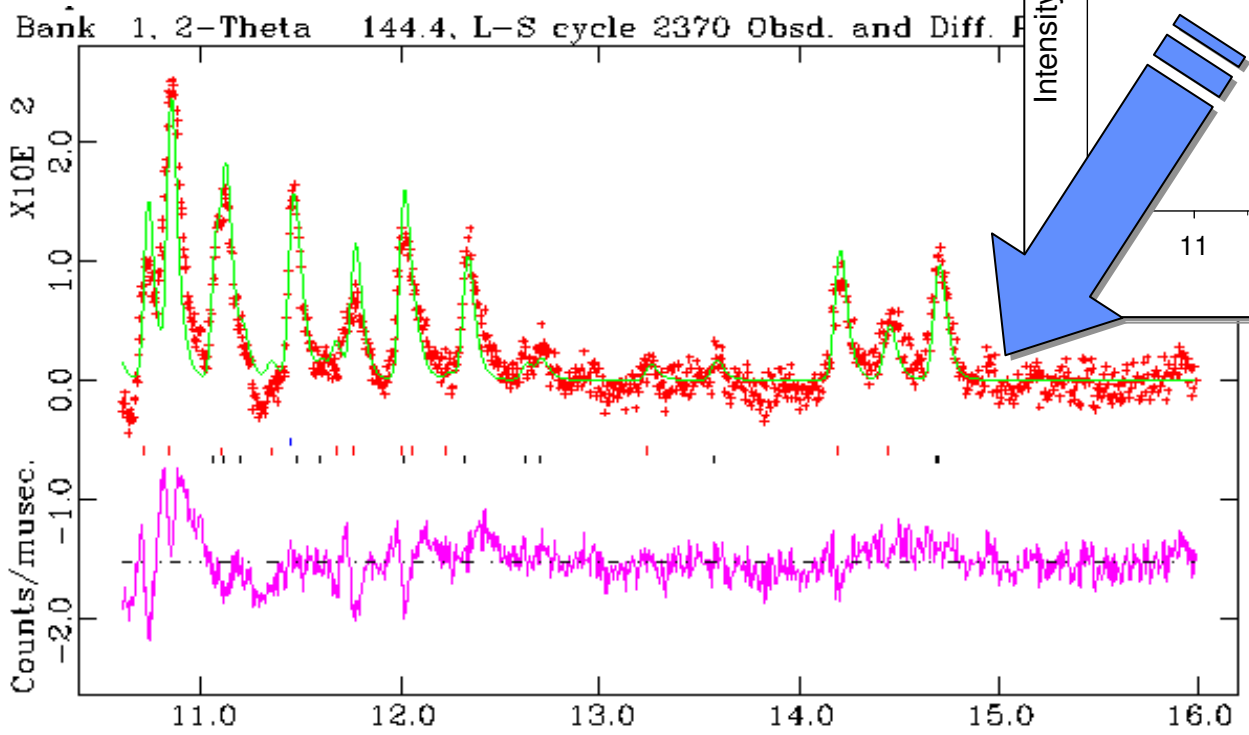
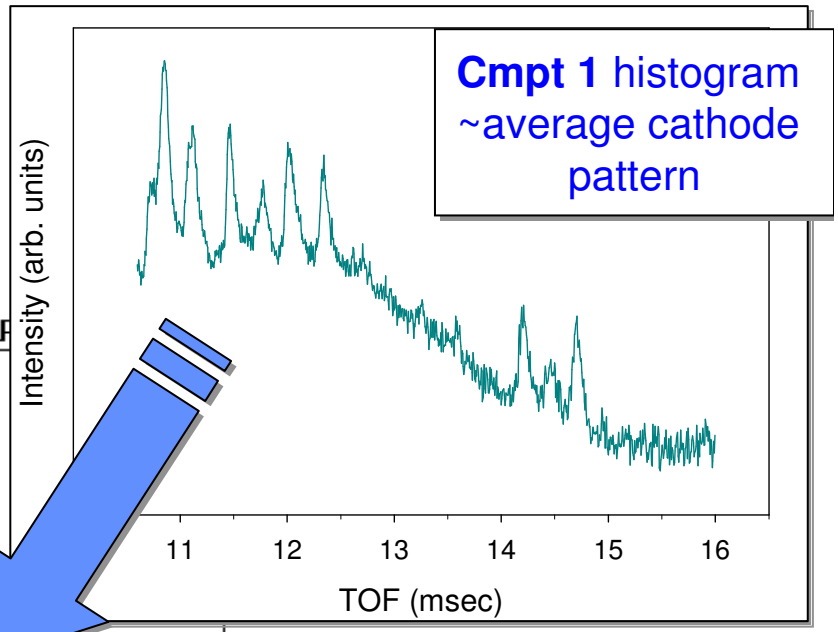


- Nishimura, et. al have performed Maximum Entropy Method (MEM) analysis of high-temperature neutron diffraction data of $LiFePO_4$
- They conclude that Li should diffuse along the b-axis via a vacant tetrahedral site adjacent to the LiO_6 octhedra

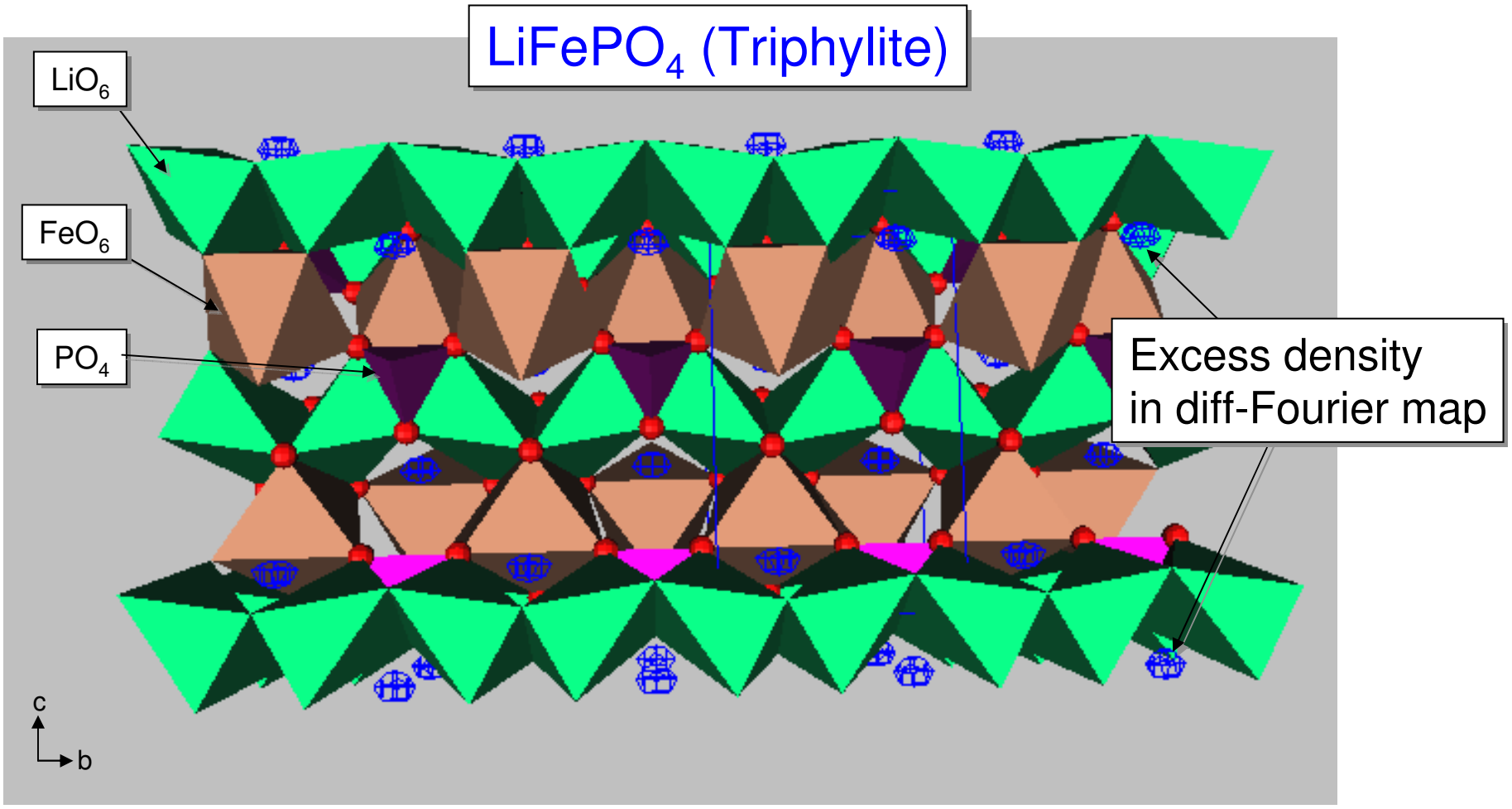
*S. Nishimura, et. al, *Nature Mater.,* **7** 707-711 (2008).

The isolated and noise-reduced **Cmpt 1** histogram was subsequently refined in GSAS.

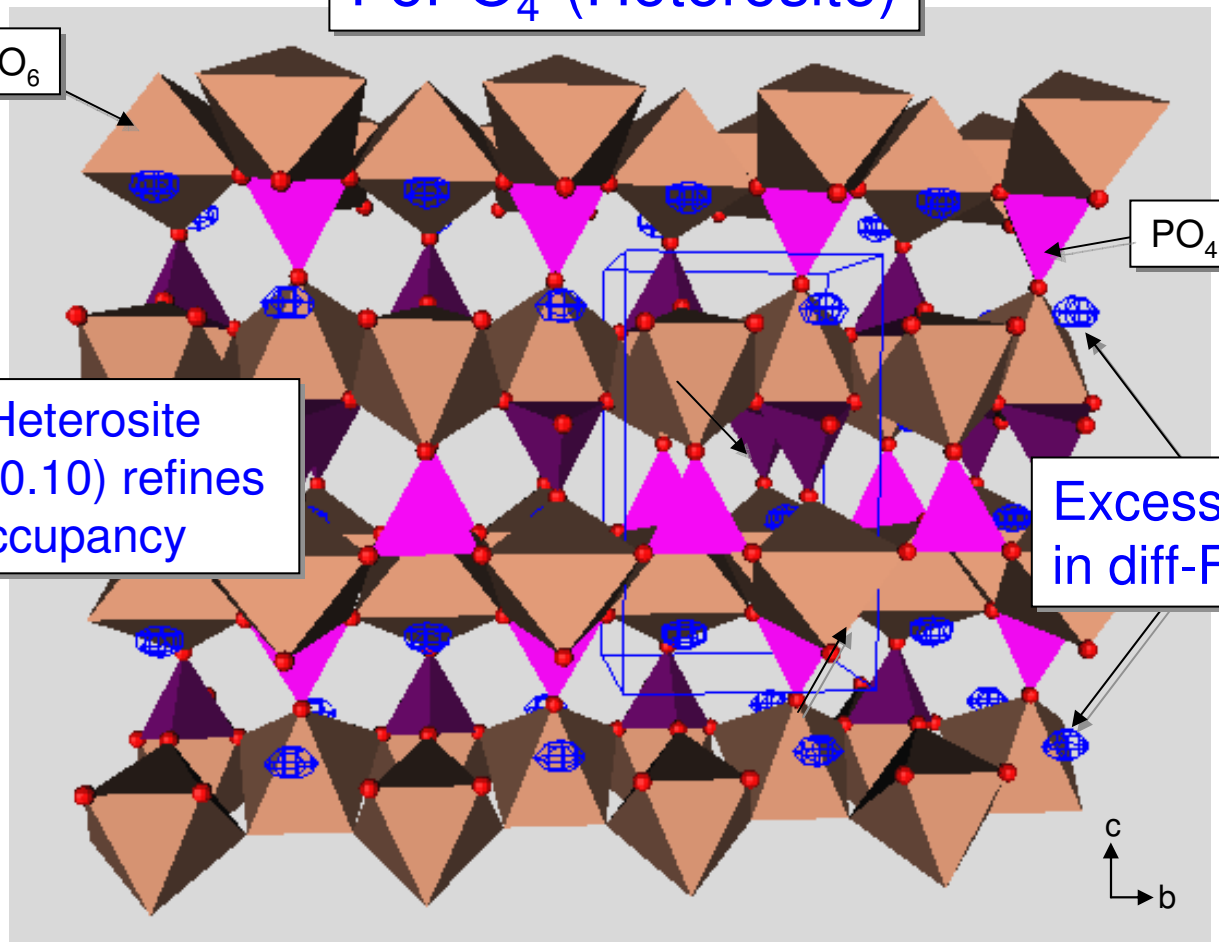




Difference-Fourier analysis of cathode phases reveals neutron density at tetrahedral site. Serendipitous result or real sensitivity to Li diffusion?



$FePO_4$ (Heterosite)



Refinement	wR_p (%)	R_p (%)	wR_p-bkg (%)	R_p-bkg (%)
no Li(tet) in Heterosite:	3.53	2.74	4.62	3.55
w/ Li(tet) in Heterosite:	3.51	2.72	4.37	3.41

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Summary

- We have successfully monitored the charge/discharge process of a commercial $LiFePO_4$ Li-ion cell using neutron diffraction.
- Principle Component Analysis successfully separated the electrochemically active phases in both anode and cathode.
  - Staging of anode phases
  - Correlation of $LiFePO_4/FePO_4$ concentration
- The battery showed significant lag when switching from the charge cycle to the 2nd discharge cycle.
- Isolation and refinement of the cathode **Cmpt 1** histogram coupled with difference-Fourier mapping suggests Li diffusion through a tetrahedral site neighboring the LiO_6 octahedra.

Acknowledgments

- **We would like to thank James Griego (SNL) and Kathy Rice (SNL) for help in preparation of this presentation.**
- Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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