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In-situ XRD Analysis of $(CF_x)_n$ Batteries: Signal Extraction by Multivariate Analysis

Mark A. Rodriguez, Michael R. Keenan,
and Ganesan Nagasubramanian

Sandia National Laboratories
Albuquerque, New Mexico 87185

National Nuclear Security Administration

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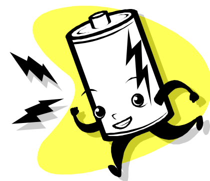
Motivation

- $Li/(CF_x)_n$ batteries have the largest theoretical specific energy and capacity of any of the ambient temperature Li-primary chemistries.
  - 2260 Wh kg^{-1}



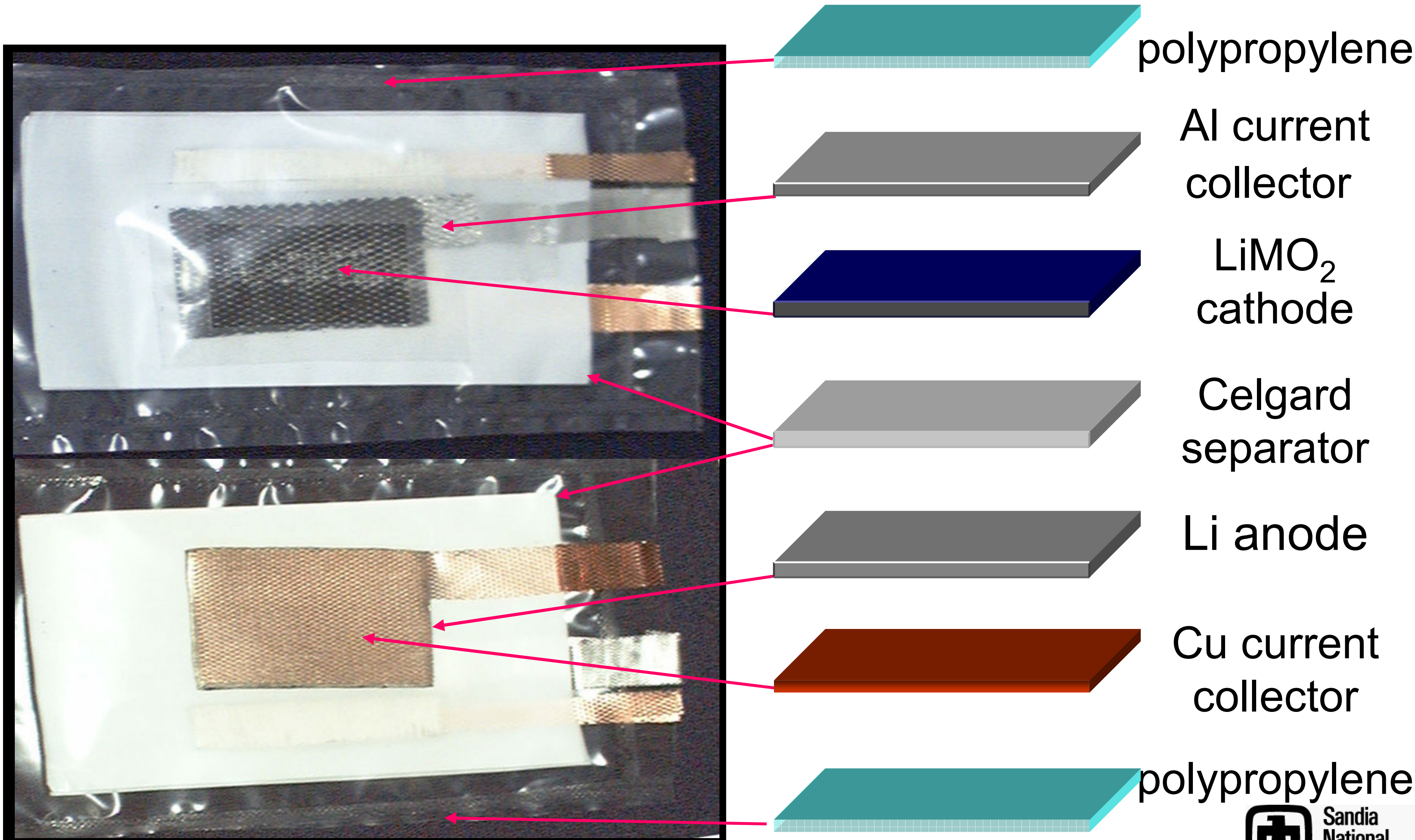
assuming one-step reaction $CF_x + xLi \rightarrow C + xLiF$

- Problem: The actual (practical) energy is only 10-35% of theoretical due to voltage drop.
  - Theoretical ~ 4.5 V, observed OCV < 3.2 V.

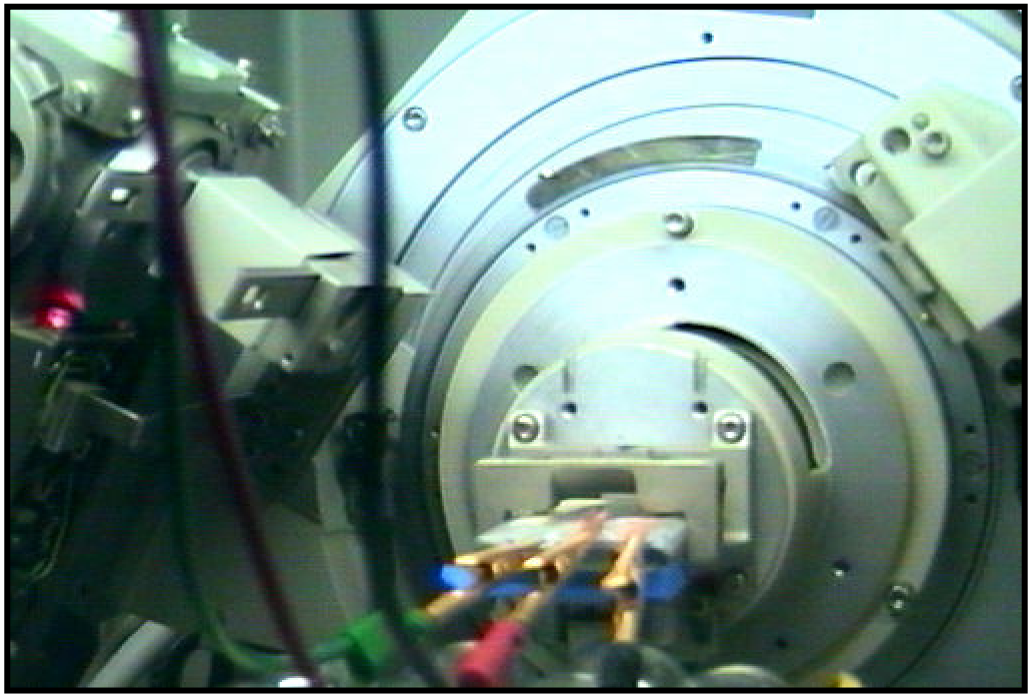
- Our LDRD program is focused on this question:
  - Can we detect any ternary compounds that control cell voltage?
    - Can we monitor the $Li/(CF_x)_n$ reaction via XRD?

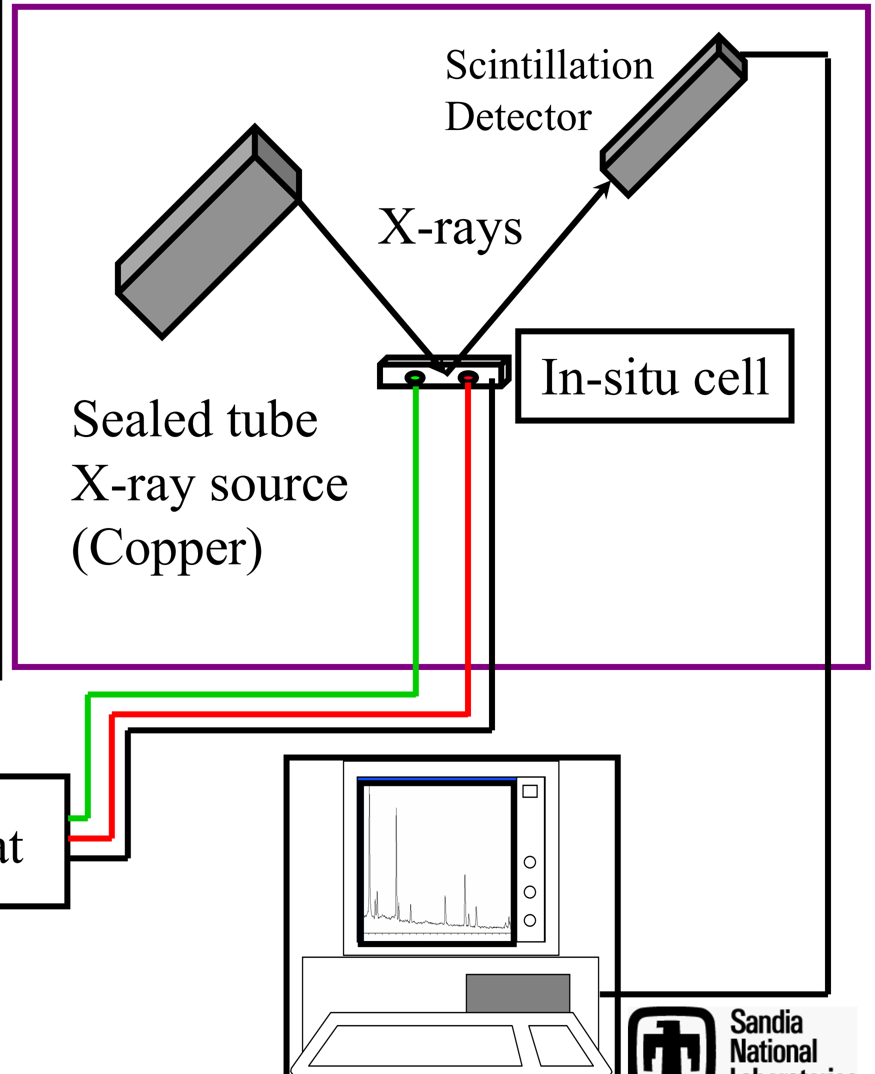
Focus of this presentation

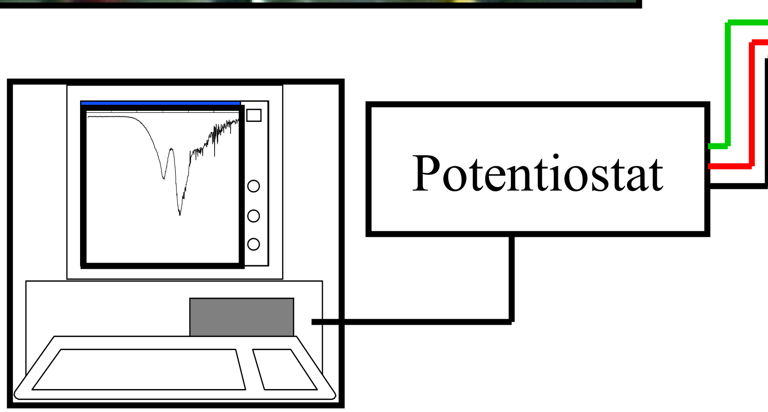
Past in-situ electrochemical experiments have employed our “*coffee bag*” type cell assembly



Schematic drawing of experimental setup indicates ease of analysis.





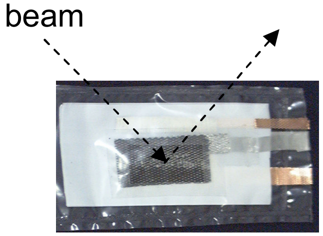


MRS Proc.
Vol. **496**,
275 (1998)

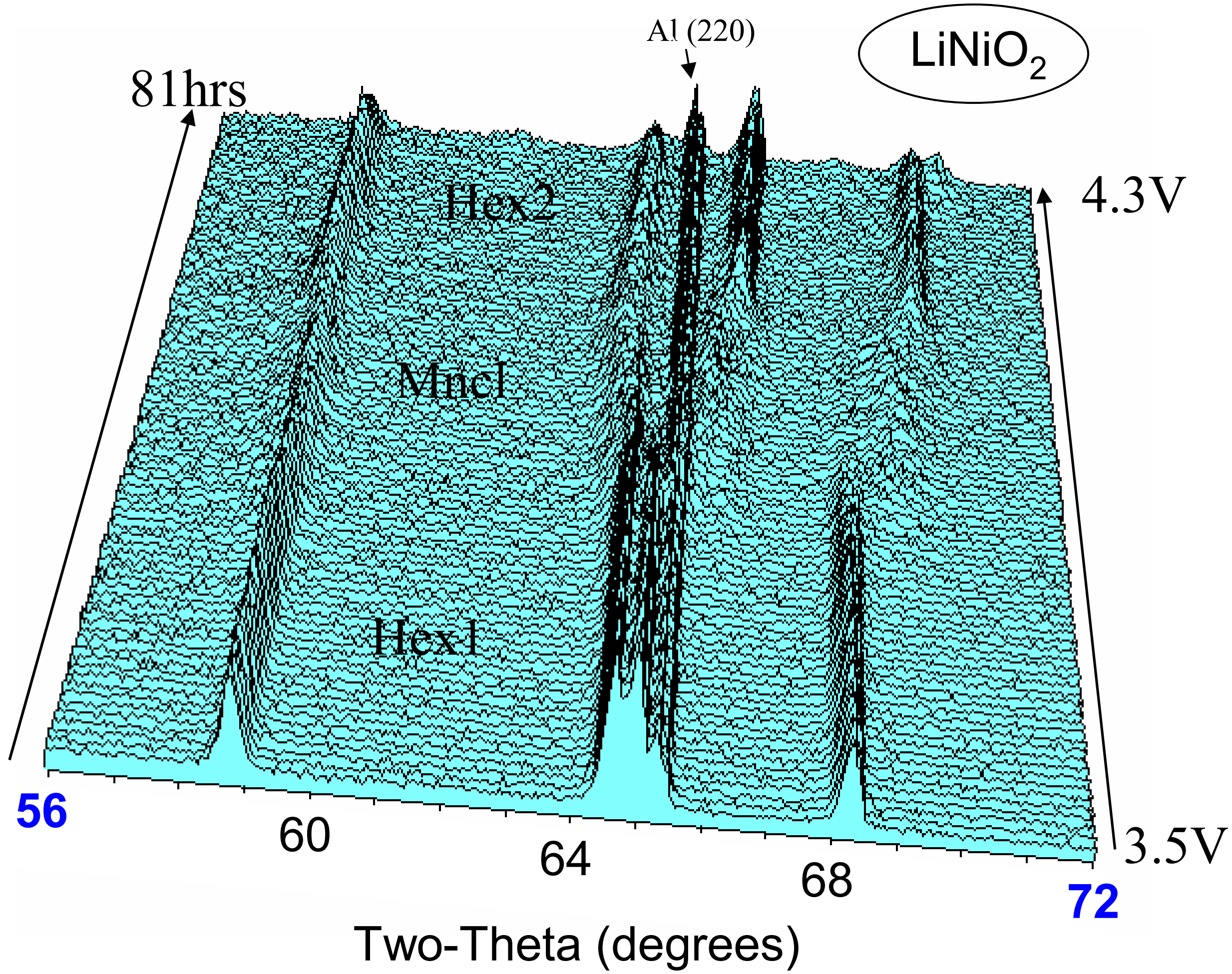
This technique worked well for well-crystallized cathode materials that have peaks at high 2θ

56-72° 2θ range is a good window for XRD analysis of $LiMO_2$.

- Lots of cathode peaks
- Just one artifact peak
  -Al (220)

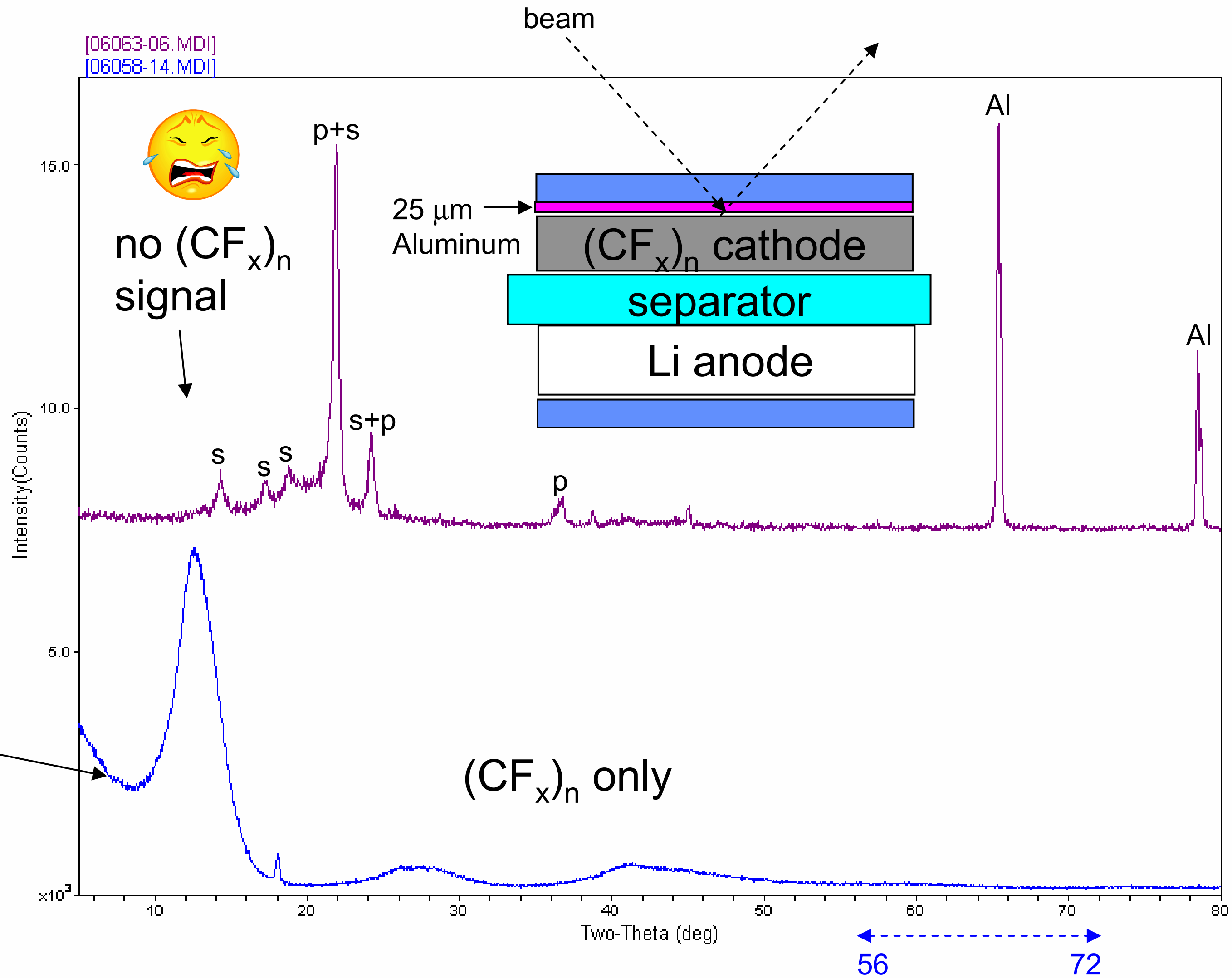


cathode side



Houston, we have a problem…

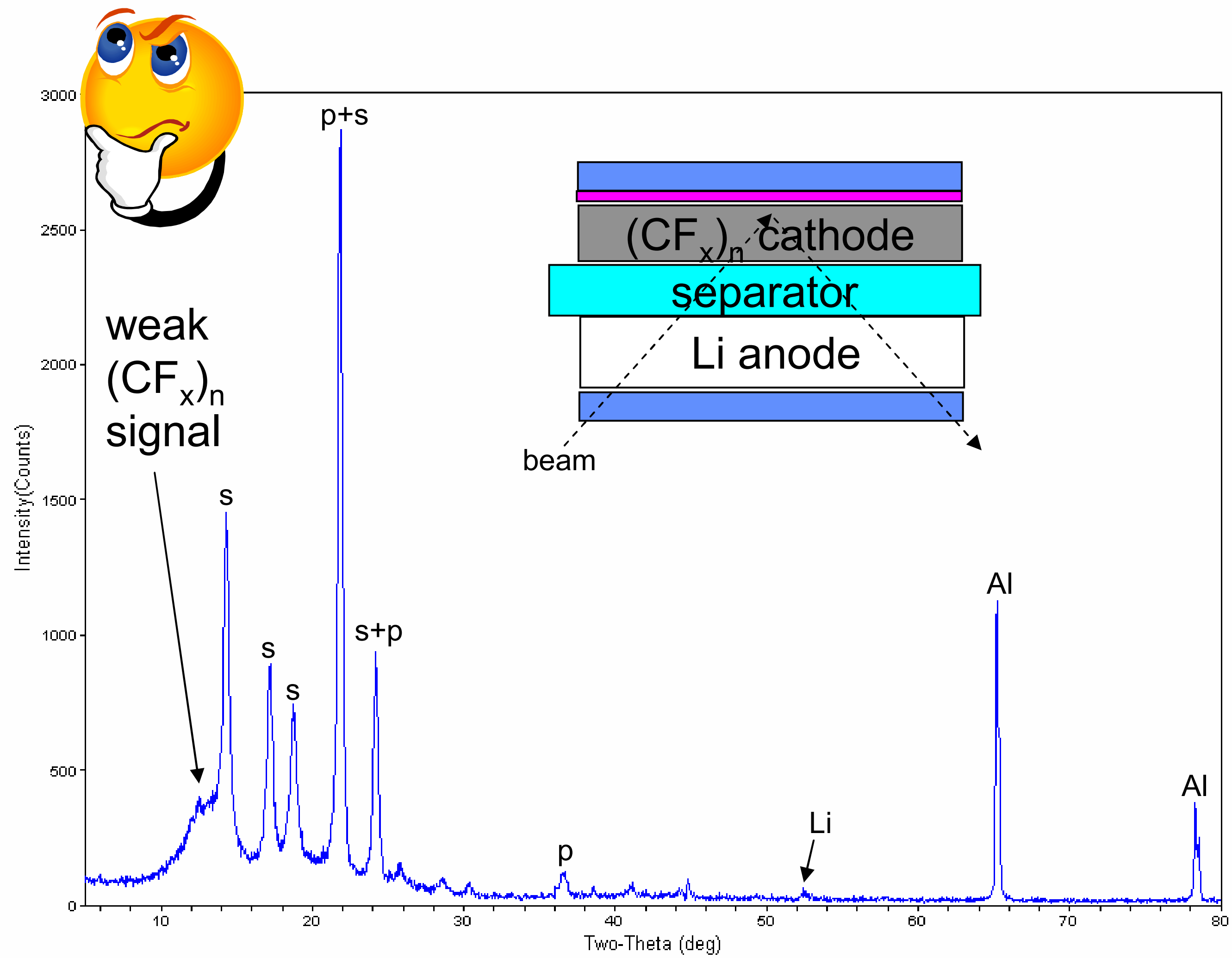
Low angles have lots of artifact peaks from the cell separator (s), plastic (p), and the 25µm Aluminum layer (current collector). XRD pattern from the assembled cell shows **no $(CF_x)_n$ signal**



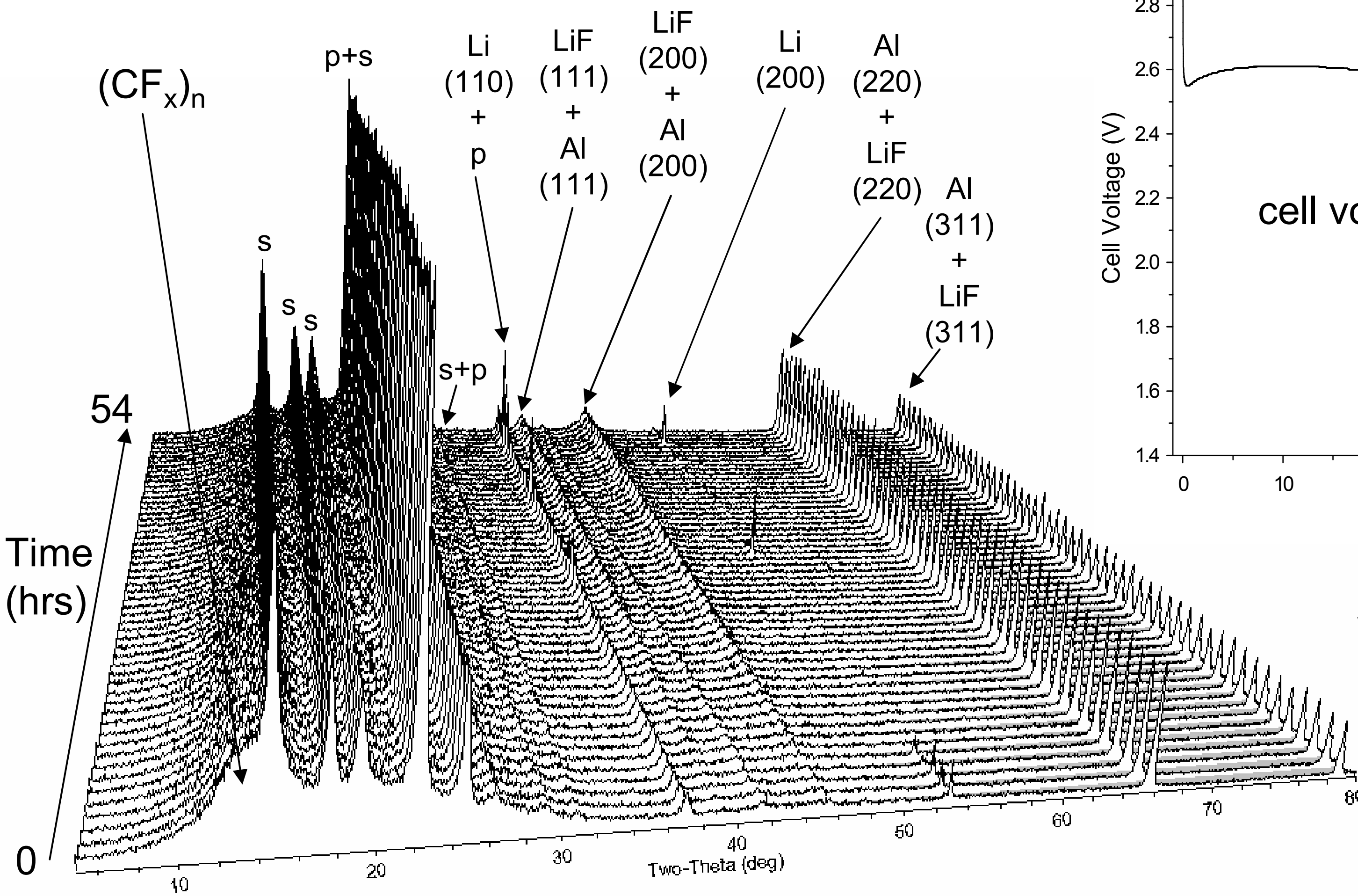
$(CF_x)_n$ cathode material has very **broad** peaks that occur at low angles

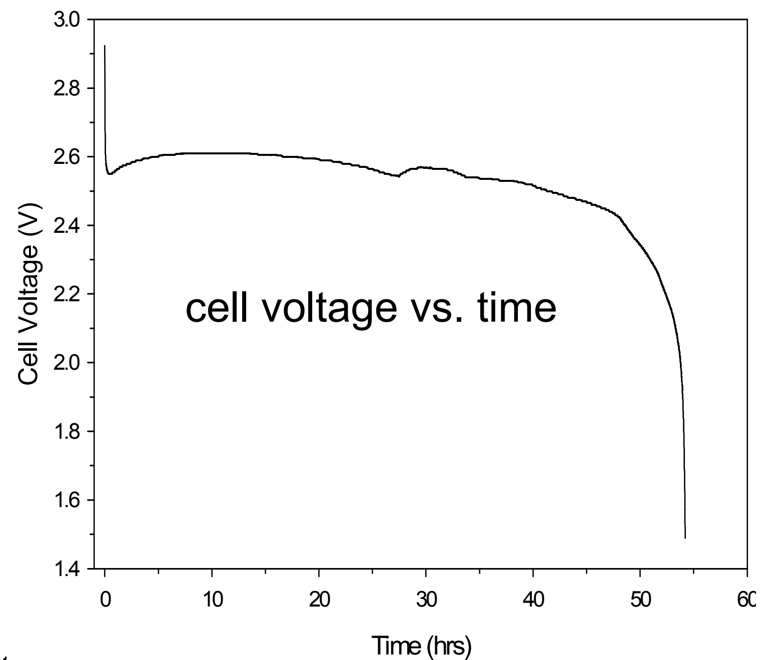
Bringing X-ray beam in from backside (through Li anode) enabled detection of $(CF_x)_n$ cathode.

With the inverted cell configuration we can at least <u>detect</u> a weak $(CF_x)_n$ signal.



We performed in-situ data collection on the inverted cell with each XRD scan ~ 1 hr. The dataset appears very convoluted.



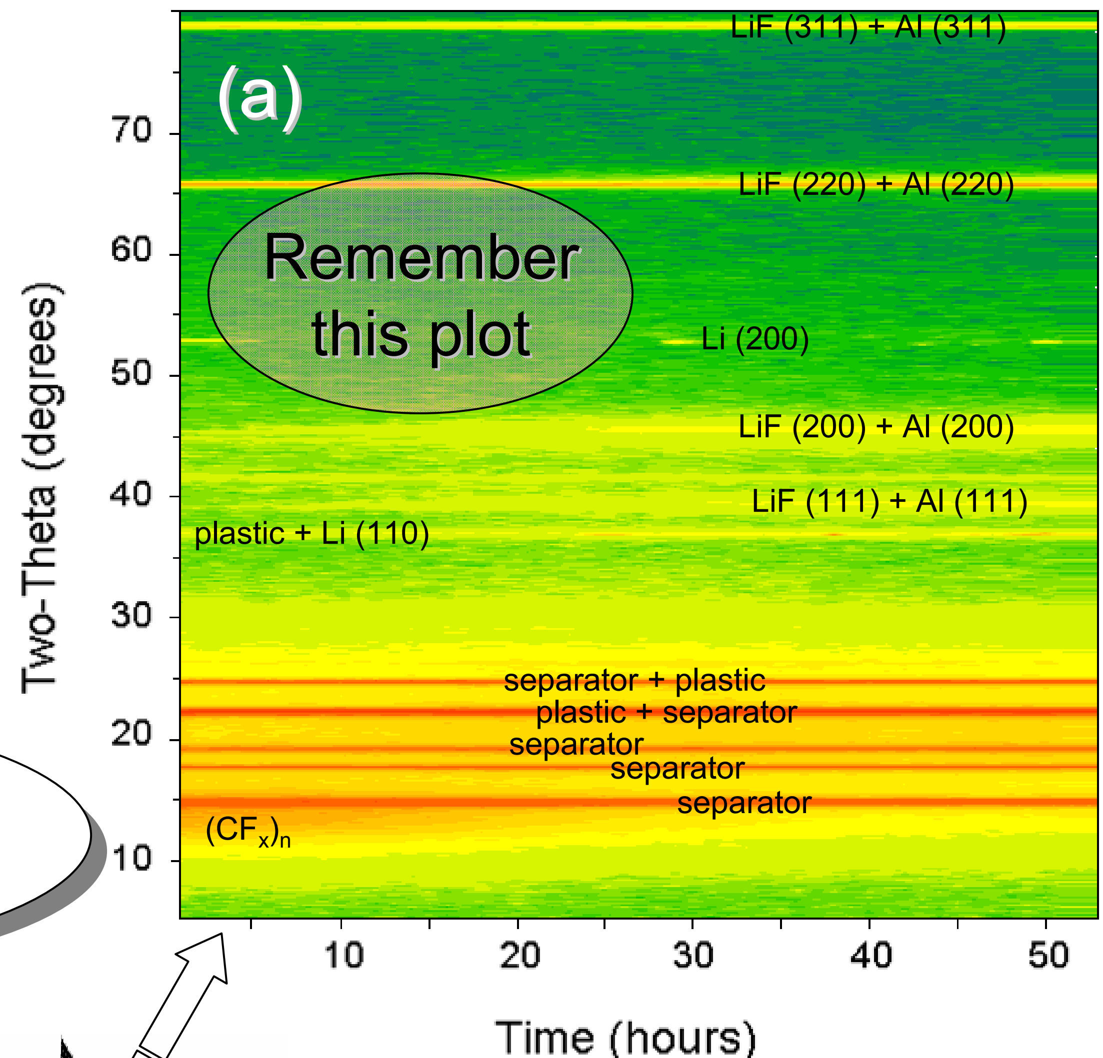


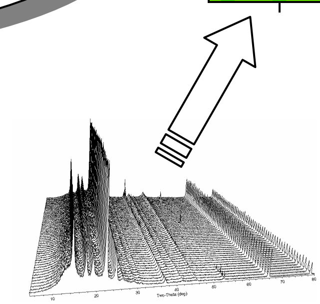
What a mess…

Contour plot of raw XRD dataset illustrates the difficulty of obtaining kinetic reaction information.

New problem:
LiF **product** peaks overlap with Al peaks.

LiF	Aluminum
Fm3m	Fm3m
a = 4.027 Å	a = 4.049 Å

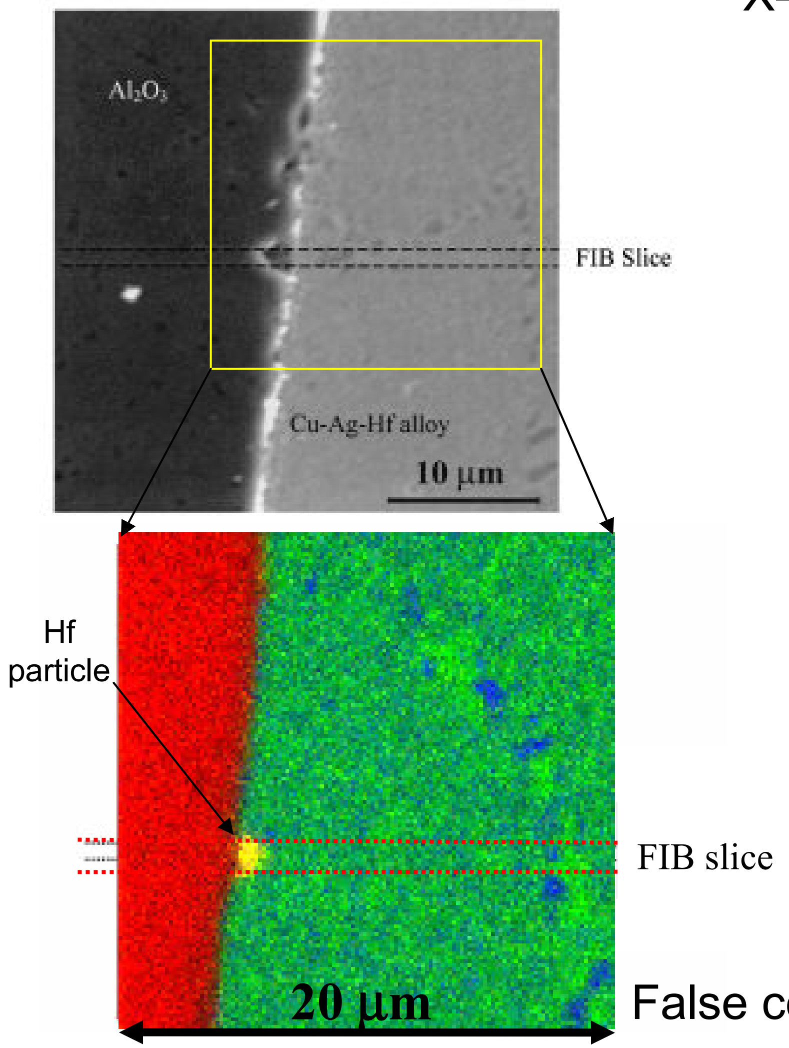




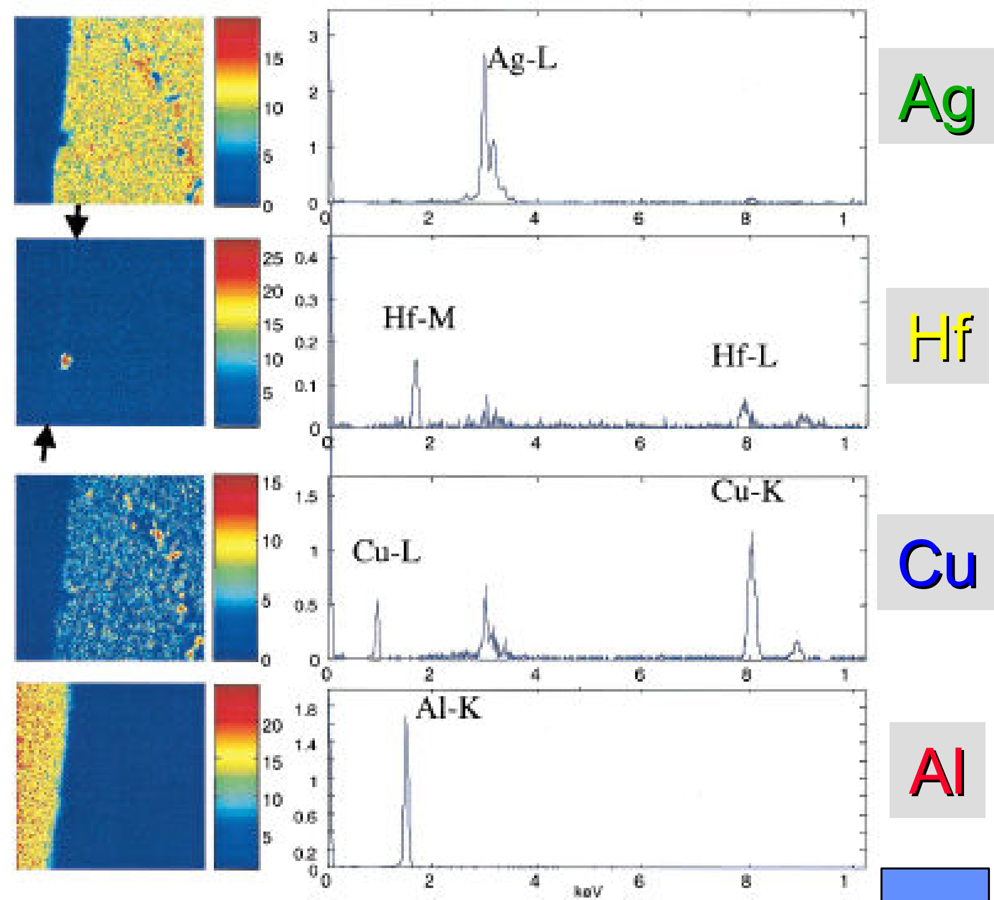
Log scale contour:
red = high intensity,
blue = low intensity

Automated Spectral Image Analysis employs MVA to generate elemental maps from massive EDAX datasets.

SEM overview



X-ray spectral image, and analysis



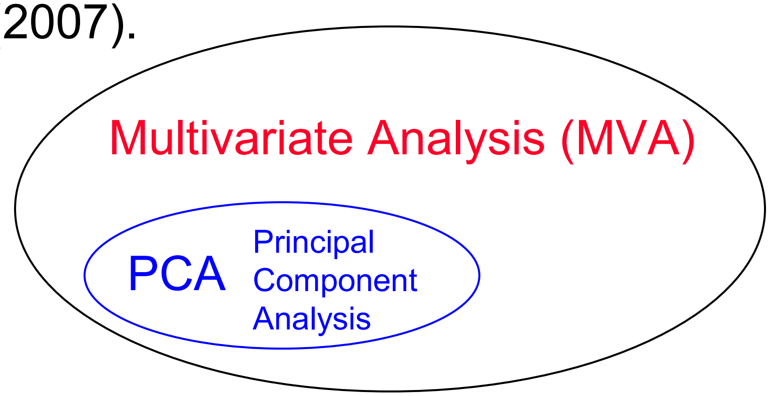
There have been a few reports demonstrating the application of Principal Component Analysis to XRD data.

‘Determination of Ammonium Nitrate in Dynamite without Separation by Multivariate Analysis Using X-ray Diffractometer’
T. Mitsui & M. Satoh, *J. Chem. Software*,* **4**, #1 (1997).

‘Enhancing the Signal-to-Noise Ratio of X-ray Diffraction Profiles by Smoothed Principal Component Analysis’
Z. P. Chen, et al, *Anal. Chem.* **77** 6563-6570 (2005).

‘The Benefits of an Integrated Full Pattern PXRD Analysis Approach’
T. Degen (PANalytical), DXC 2006, Abstract D099, pp 120.

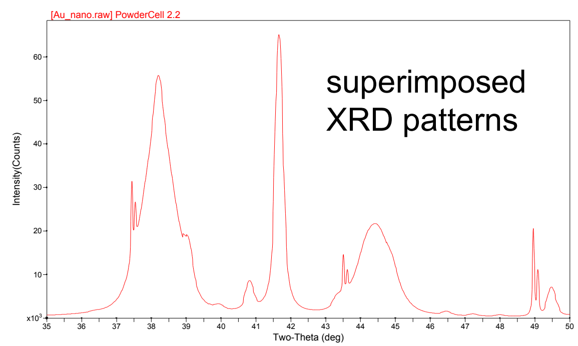
‘Principal Component Analysis of X-ray Diffraction Patterns to Yield Morphological Classification of Brucite Particles’
C. Matos, et al, *Anal. Chem.* **79** 2091-2095 (2007).

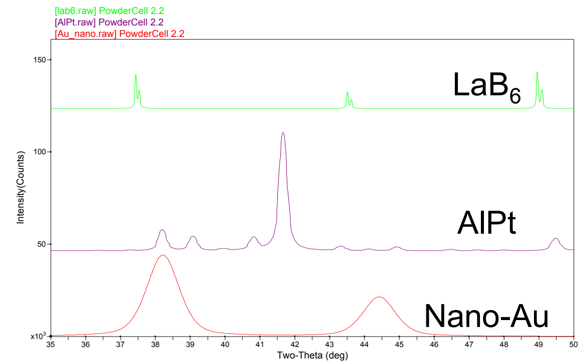


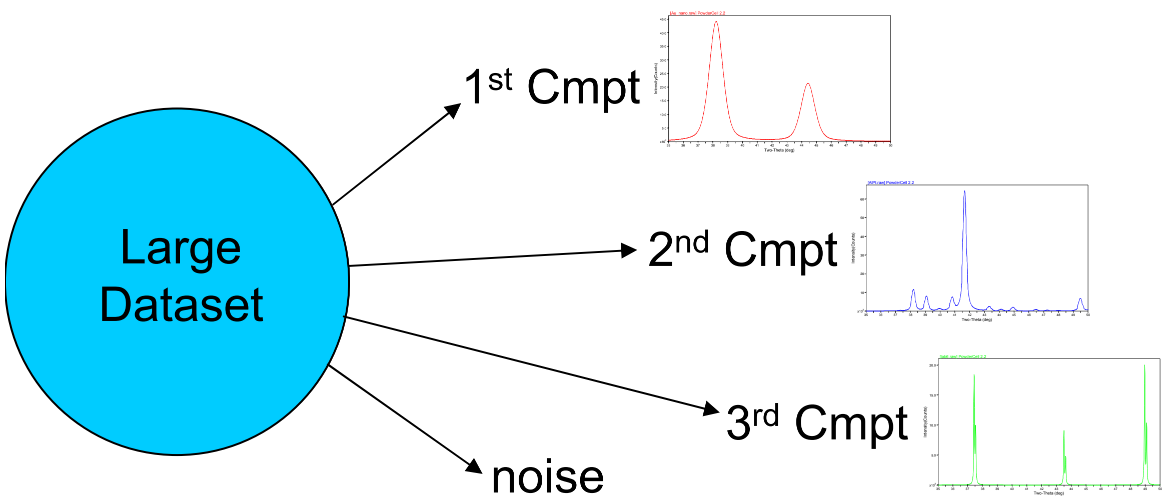
*Online Journal for the Society for Computer Chemistry, Japan (SCCJ)

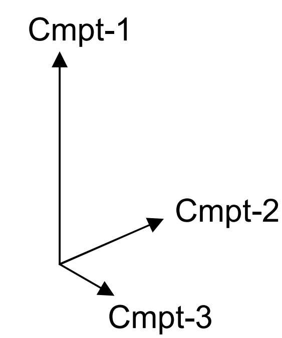
Principal Component Analysis (PCA) is the most common form of Multivariate Analysis (MVA).

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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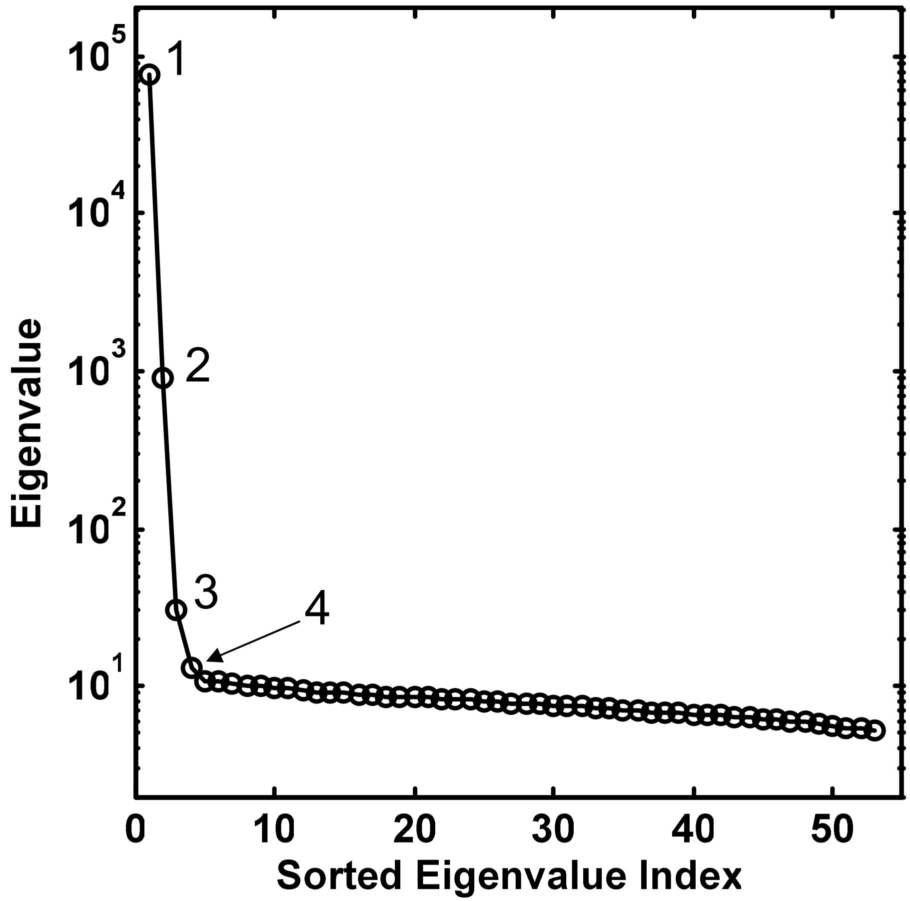
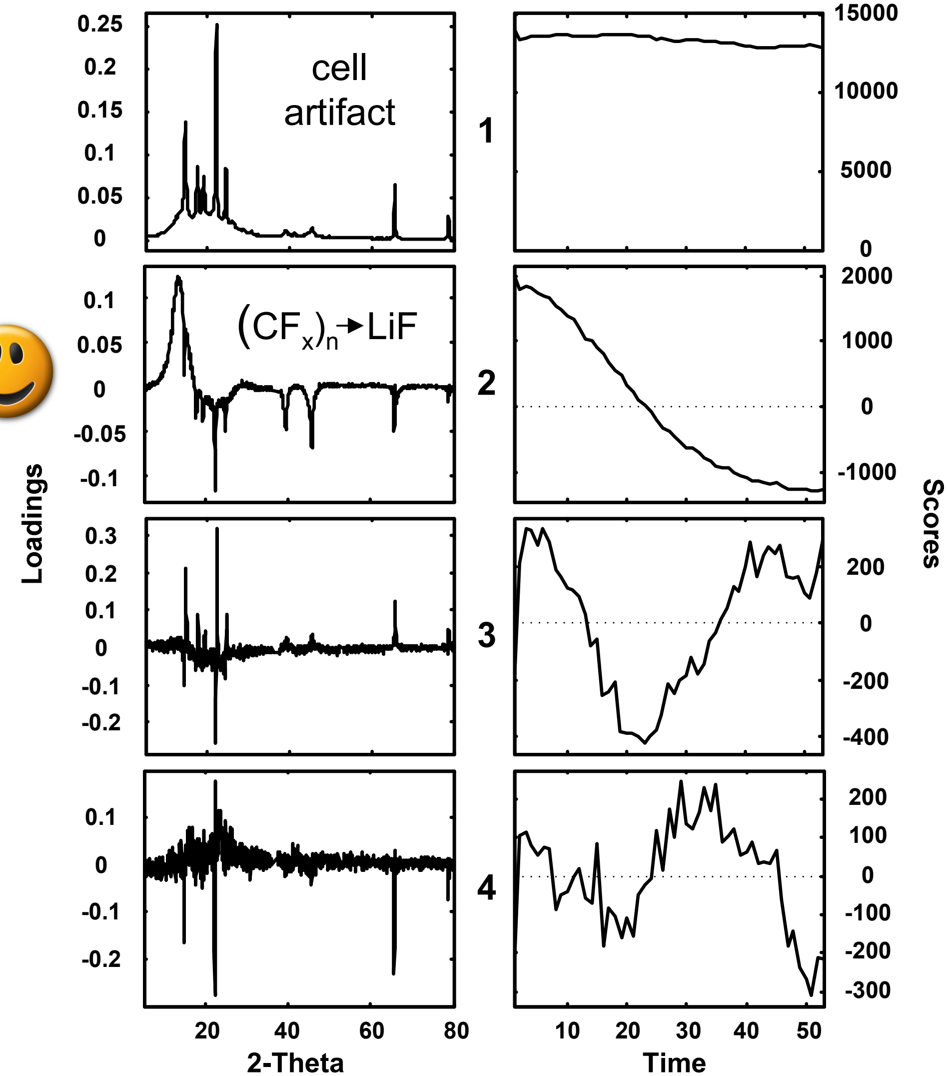
The preliminary PCA analysis shows sensitivity to intensity from the electrochemical reaction.



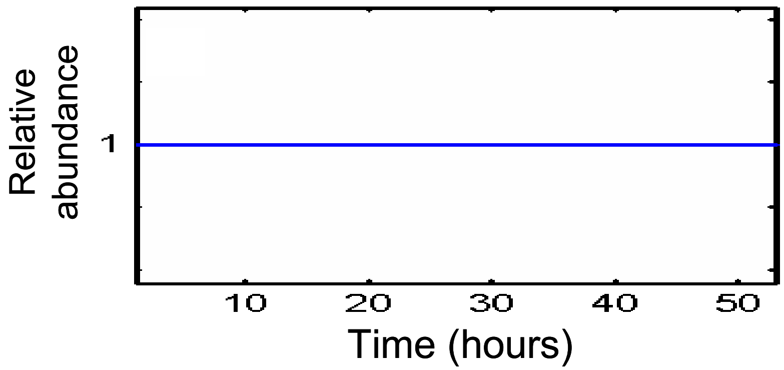


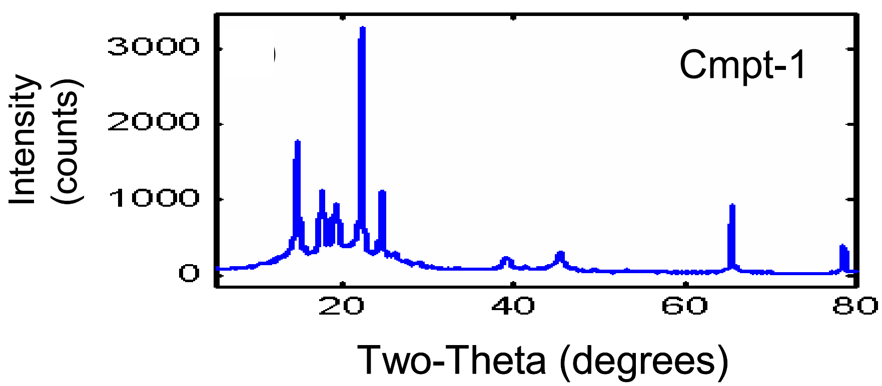
Data scaled for non-uniform noise:
Keenan & Kotula (2004). *Appl. Surf. Sci.*, **231-2** 240-244.

We improved our analysis by using Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS)

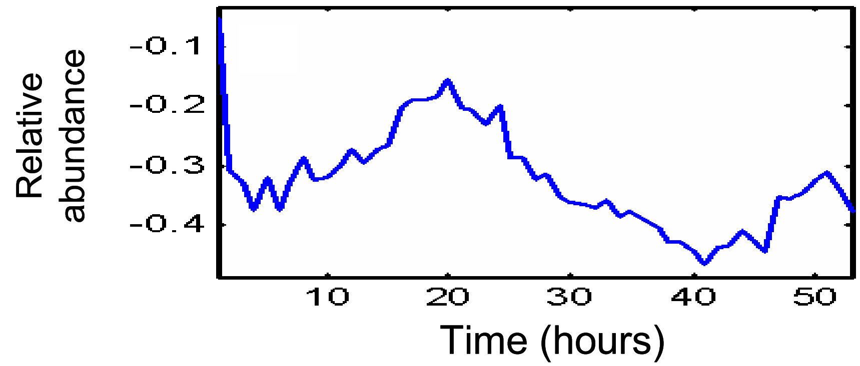
MCR-ALS employs *physically plausible constraints* to improve assessment & interpretation of the components.

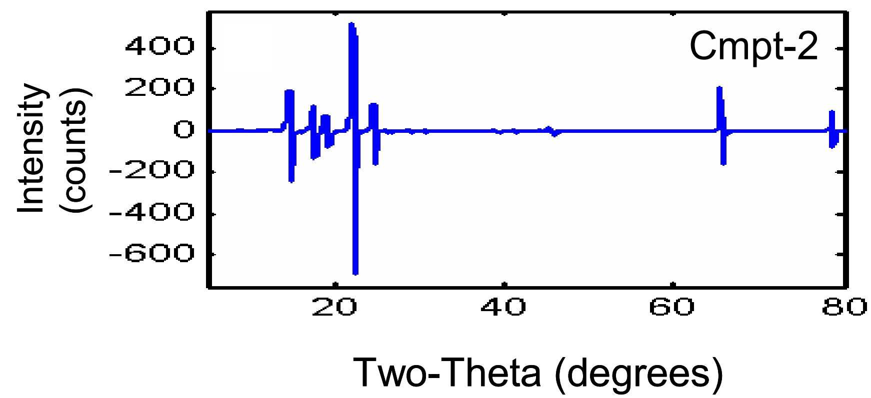
Cmpt 1 - Cell artifact





Cmpt 2 - displacement





Cmpt 1 + Cmpt 2 = "**Inert**" component (**I**-Cmpt)

Assumption: Intensity constant but free to shift in 2θ.

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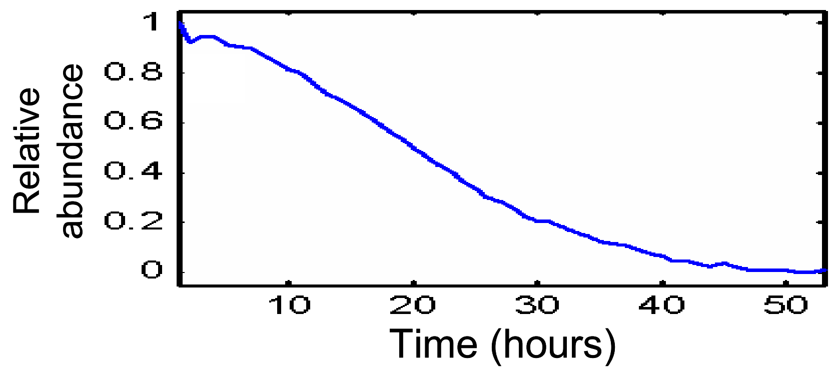
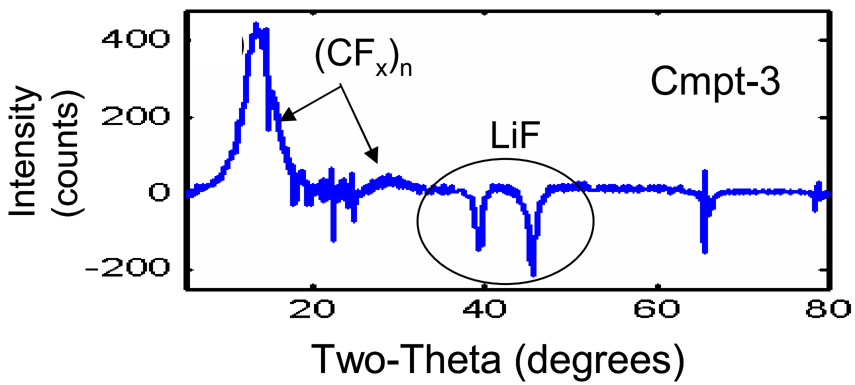
The remaining two components yield 'dynamic' information about electrochemical reaction.

Assume: same time dependence

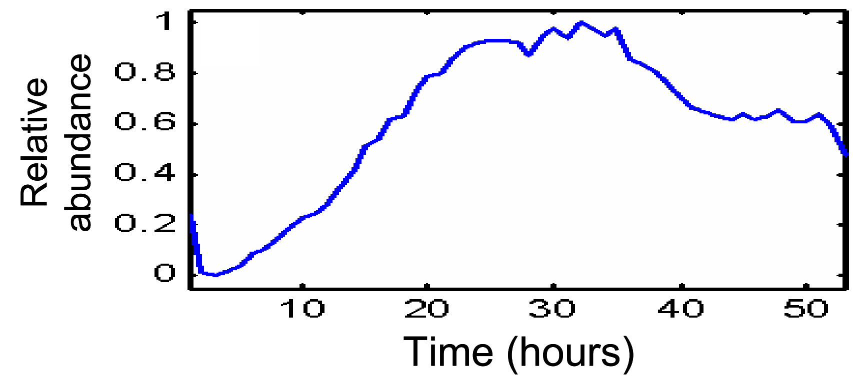
Cmpt 3 $[(CF_x)_n] \propto -[LiF]$

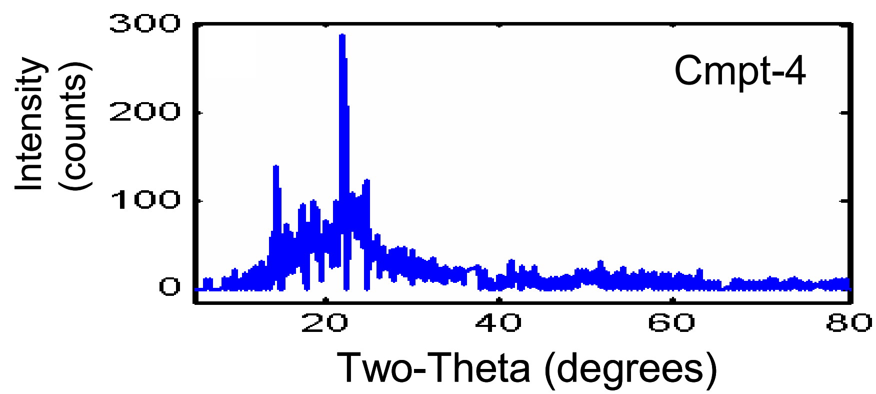




Assume: non-negative

Cmpt 4 – "intermediate"?





The weak forth component (Cmpt 4) implies that there is an additional species present during discharge.

The following researchers have speculated about an intermediate intercalation compound (e.g. $CF_{(x-y)}$-Li^{+}) existing in CFx type electrochemical cells.

Guerin, K., Dubois, M., & Hamwi, A. (2006). *J. Phys. Chem. Solids*, **67**, 1173-1177.

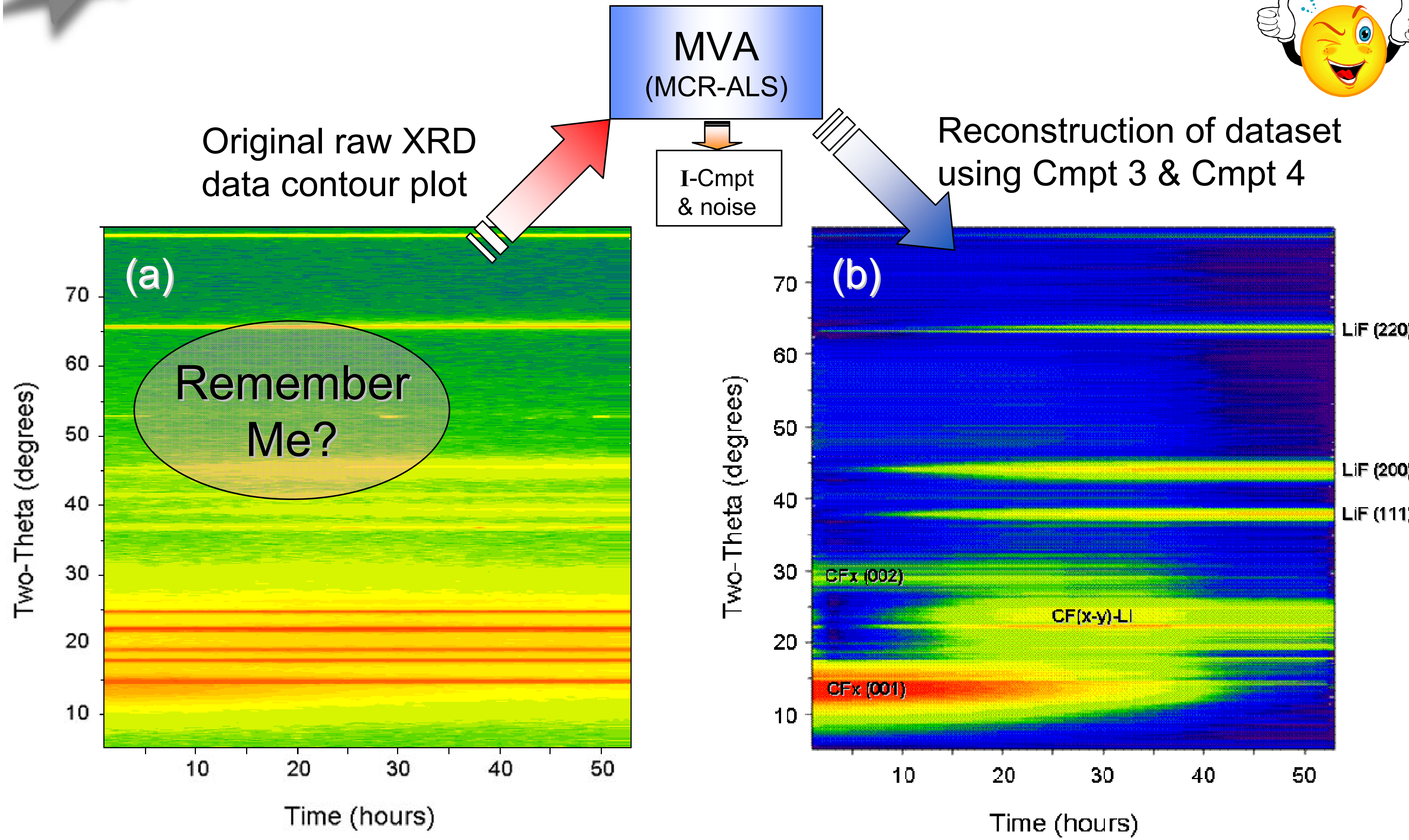
Hagiwara, R., Nakajima, T., & Watanabe, N., (1988). *J. Electrochem*. Soc., **135**, 2128-2133.

Touhara, H., Fujimoto, H., Watanabe, N., & Tressaud, A. (1984). *Solid State Ionics*, **14**, 163-170.

Whittingham, M. S. (1975). *J. Electrochem. Soc*., **122**, 526-527.

We shall discuss the 4th component as $CF_{(x-y)}$-Li^{+}

We can now reconstruct the dataset with exclusion of the I-Cmpt to view the electrochemical behavior.



Log scale contours: red = high intensity, blue = low intensity

Conclusions

- **We have successfully applied Multivariate Analysis (MVA) to in-situ XRD data for the extraction of electrochemical reaction information.**
- **During cell discharge, $(CF_x)_n$ decomposition directly correlates to the formation of LiF (i.e. Cmpt-3).**
- **We observed a weak component (Cmpt-4) which obtains maximum concentration at the midpoint of cell discharge.**
- **We have tentatively identified Cmpt-4 as an intermediate intercalation phase.**
  - **possible composition $CF_{(x-y)}$-Li^+**
- **MVA holds promise for future analysis of large XRD datasets.**

Acknowledgments

- **Bryan Sanchez (SNL) for fabrication of the "coffee bag" electrochemical cell.**
- **Paul Kotula (SNL) for the example of MVA applied to EDAX datasets.**

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