

# ▶ Operando Diffraction During Battery Operation using Lab, Synchrotron X-Ray and Neutron Diffraction

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F. Chen, E. Suard, F. Fauth, J. B. Leriche  
and L. Croguennec

ANF Réciprocs 2018





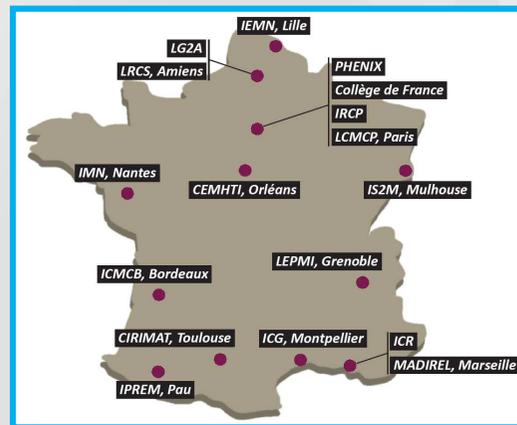
# THE FRENCH NETWORK ON ENERGY STORAGE

# The French Network on Energy Storage

## ▶ GOALS

- Resolve scientific deadlocks and achieve breakthroughs in the field of batteries and supercapacitors for stationary and mobile applications
- Improve tech-transfer between research labs and companies

[www.energie-rs2e.com](http://www.energie-rs2e.com)



## ▶ MEMBERS

- 17 Laboratories (150 researchers + 75 students)
- 3 public organizations (CEA, INERIS and IFPEN)
- 15 Industrial Partners (Alstom, EDF, Renault, Solvay, Total, Zodiac Aerospace, SAFT, Solvionic, Aurock, E4V, EasyLi, Freemens, Tiamat)

## ▶ COORDINATED BY:

Pr. Jean-Marie TARASCON

Pr. Patrice SIMON and 10 senior researchers since 2011

# The French Network on Energy Storage



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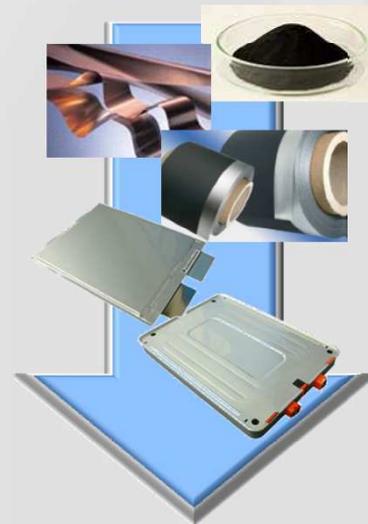
## ▶ 2 GOALS

- PASS QUICKLY FROM THE CONCEPT TO THE PROTOTYPE(S)
- BUILD A PATENT PORTFOLIO



## ▶ APPLIED RESEARCH AND TECH-TRANSFER

- Product-centered approach (TRL)
- Battery pilot-line (characterization, prototyping, test)
- Vast knowledge of synthesis and upscaling (up to pack assembly)



COLLÈGE  
DE FRANCE  
1530



## ▶ ACADEMICS' EXPERTISE:

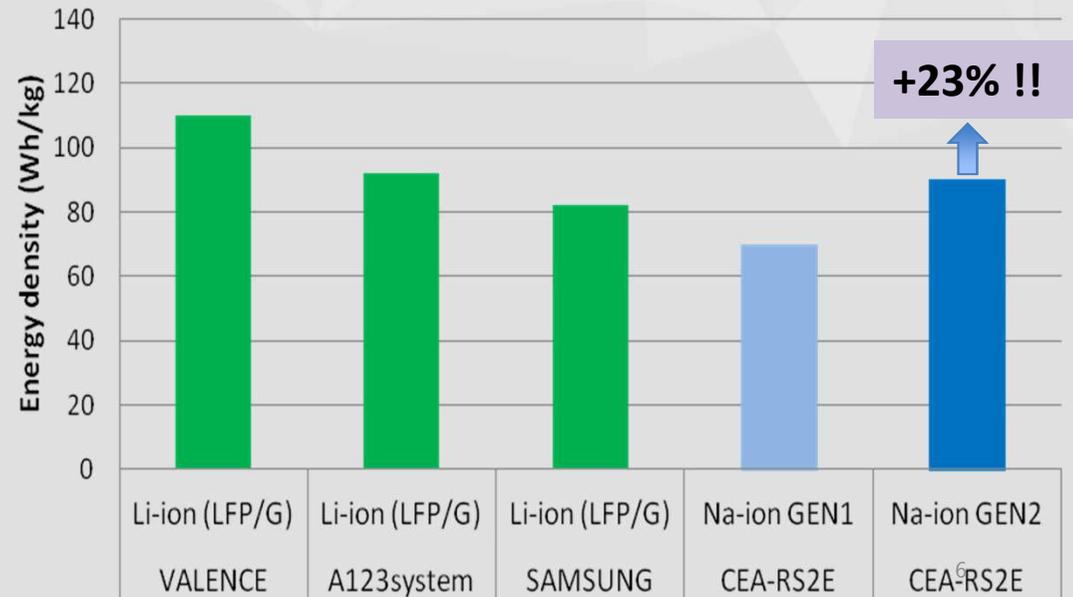
- Design and development of new materials for Na-ion batteries
- Advanced characterization techniques

# Main Results on Na-ion Technology

- ▶ Na-ion technology can have performances close to Li-ion's (cyclability, power, charge retention...)
- ▶ Simple fabrication process (similar to Li-ion)
- ▶ Huge interest regarding criticality of raw materials supply
- ▶ Cost analysis : lower price of Na-ion confirmed

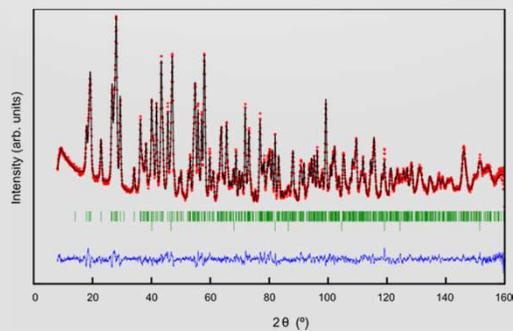
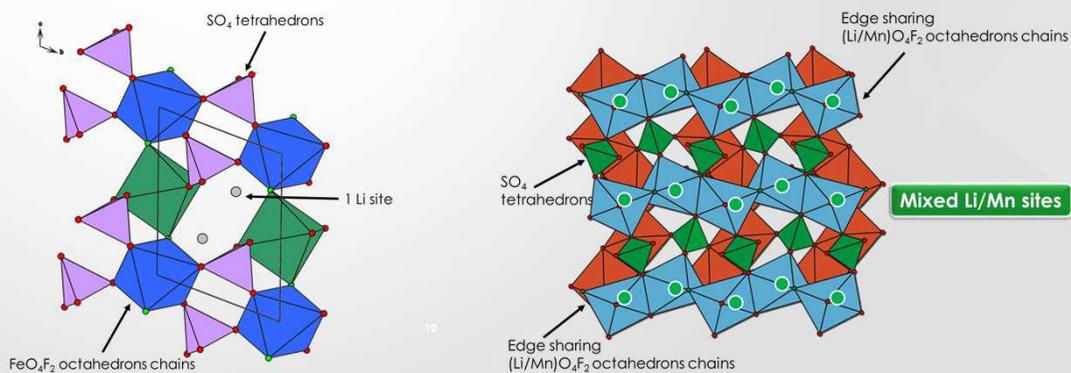


90 Wh/kg - 180 Wh/L



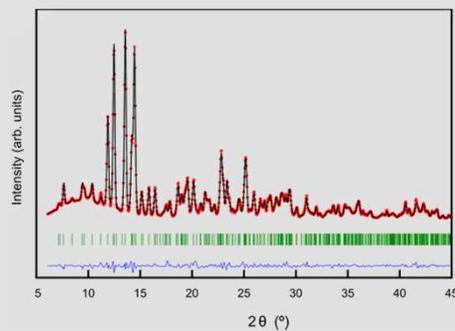
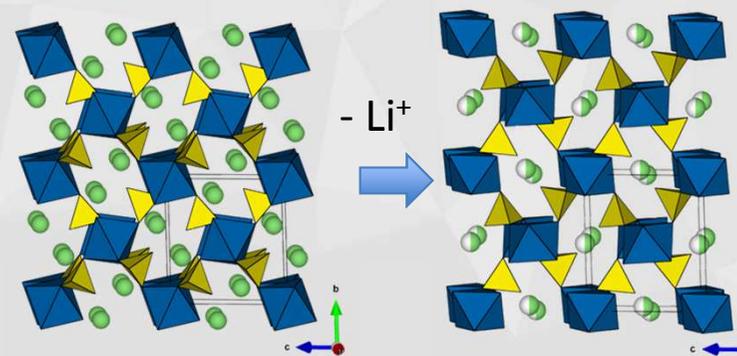
# Research at LRCS : a short overview

## Tavorite / Triplite: $\text{LiFeSO}_4\text{F}$

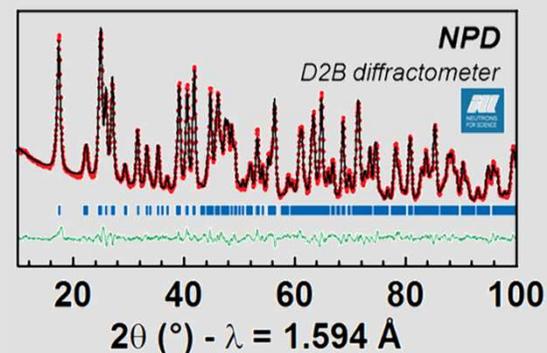


N. Recham, *et al*, Nature Materials, 2010, 9, 68-74,

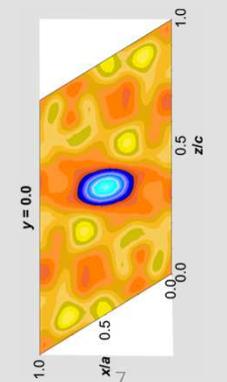
## Marinite: $\text{Li}_2\text{M}(\text{SO}_4)_2$



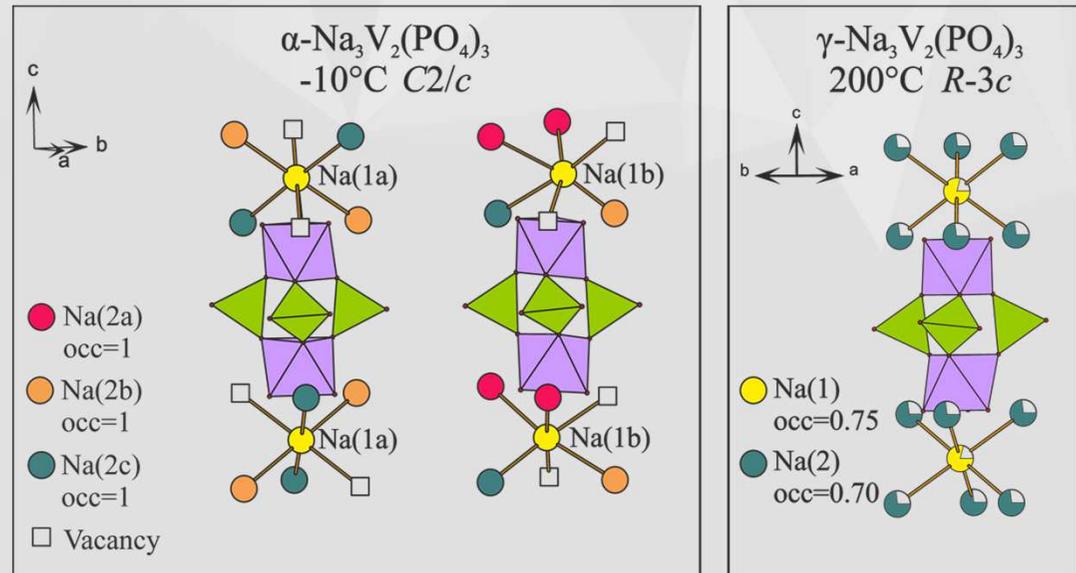
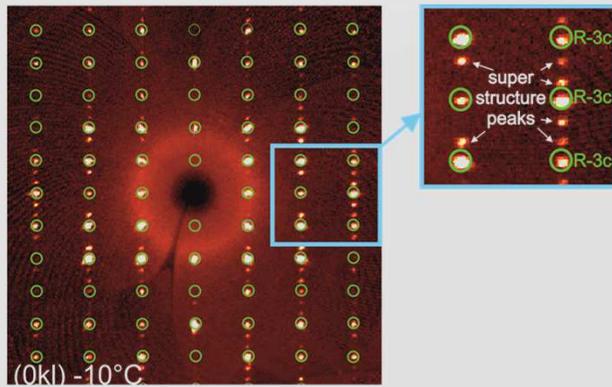
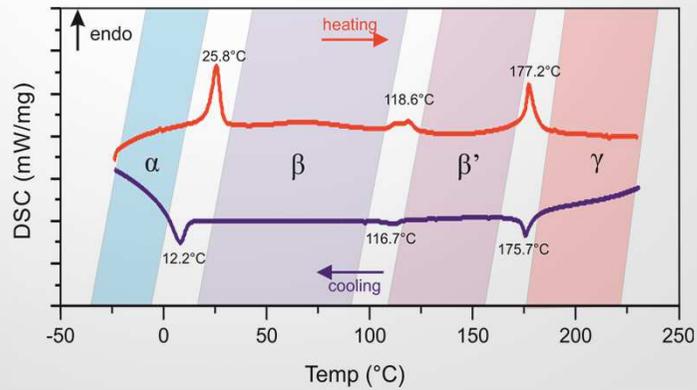
Barpanda *et al*, Nature Materials, 2011, 10, 772-779



Reynaud *et al*. Electrochem. Commun. 2012 ; Reynaud *et al*. Patent FR 12 51854.

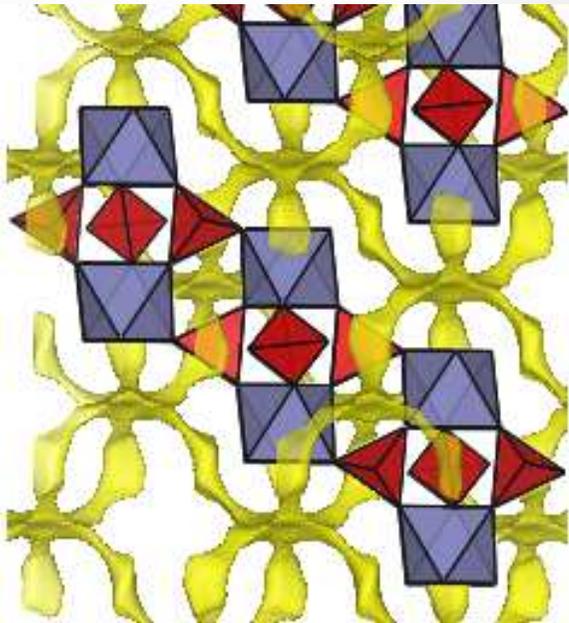


# Research at LRCS : a short overview

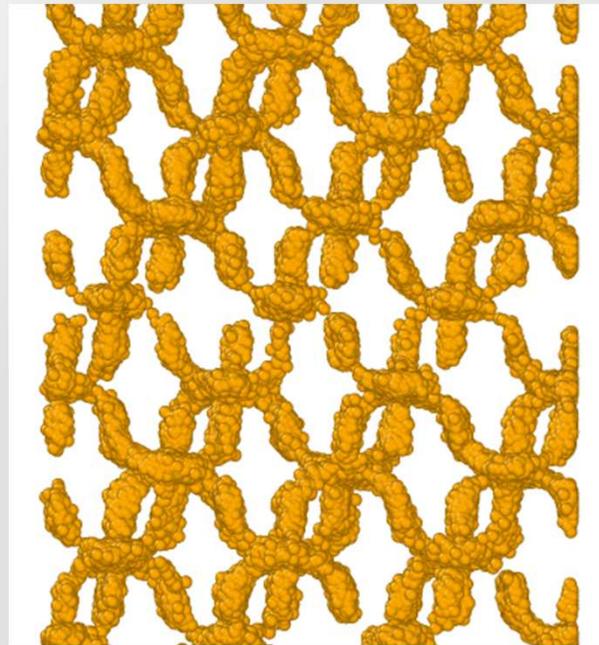


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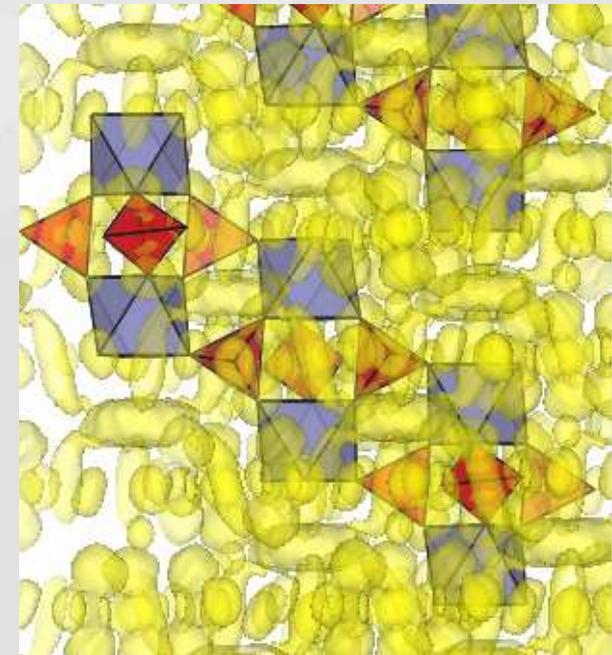
NASICON:  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  solid electrolyte diffusion pathway



Bond Valence Energy  
Landscape (1eV)



MD snapshots over 1  
nanosecond (every 1 ps)

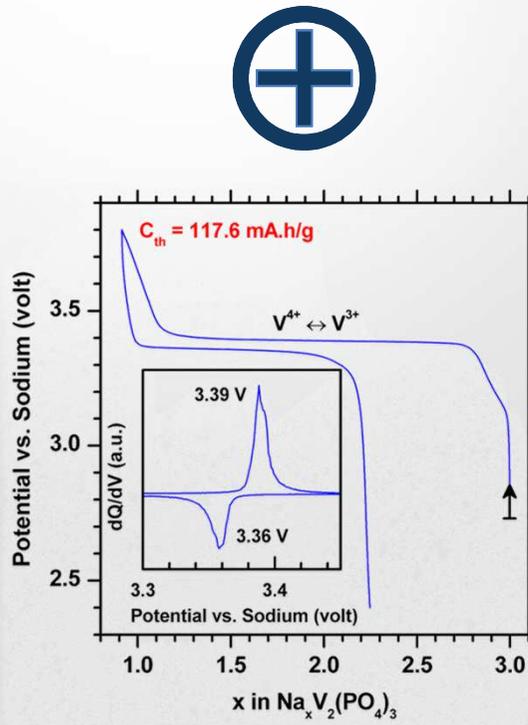


Maximum Entropy  
Method / Rietveld<sup>9</sup>

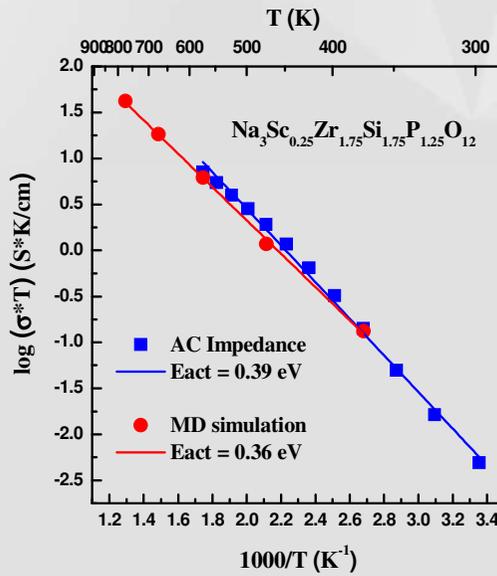
# Research at LRCs : an short overview

NASICON: All Solid State Batterie

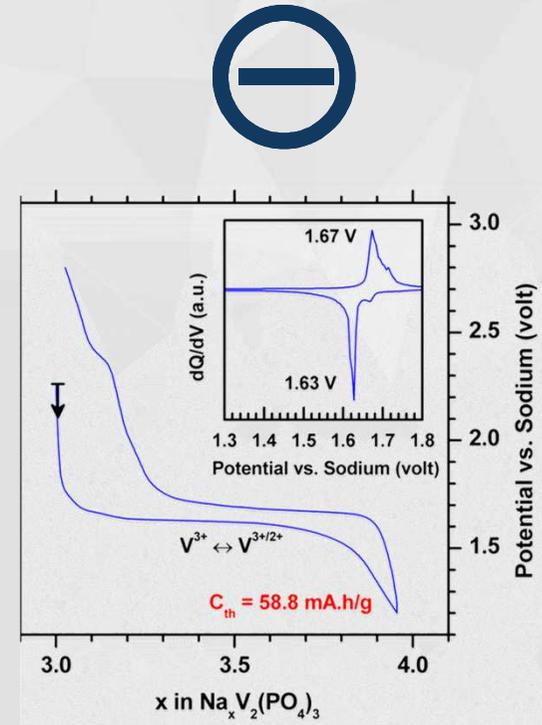
## Electrolyte



$\text{Na}_3\text{V}_2(\text{PO}_4)_3$   
(NVP)



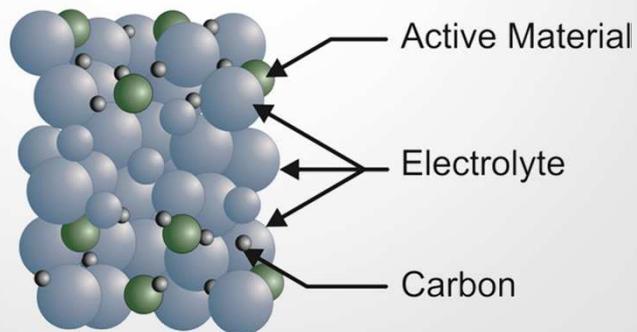
$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$   
(NZSP)



$\text{Na}_3\text{V}_2(\text{PO}_4)_3$   
(NVP)

# ALL-NASICON Battery

## Design:



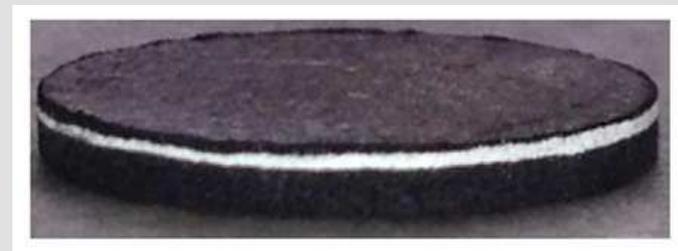
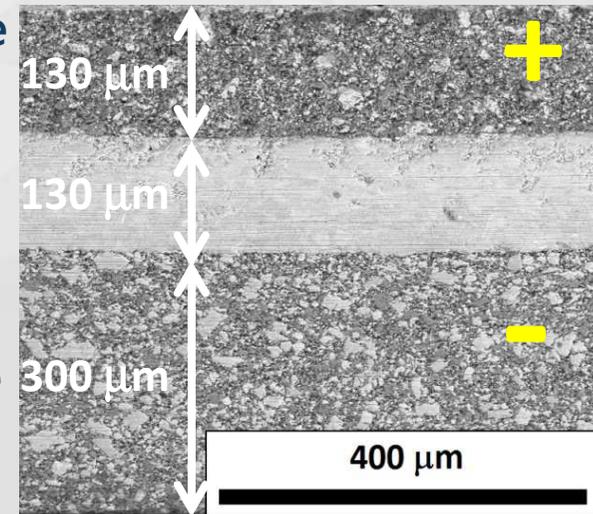
## Preparation:

- Stacking by cold-press
- Sintering by SPS at 900°C
- Monolithic Full Solid State Battery

Composite electrode  
NVP/NZSP/C<sub>sp</sub>

Electrolyte  
NZSP

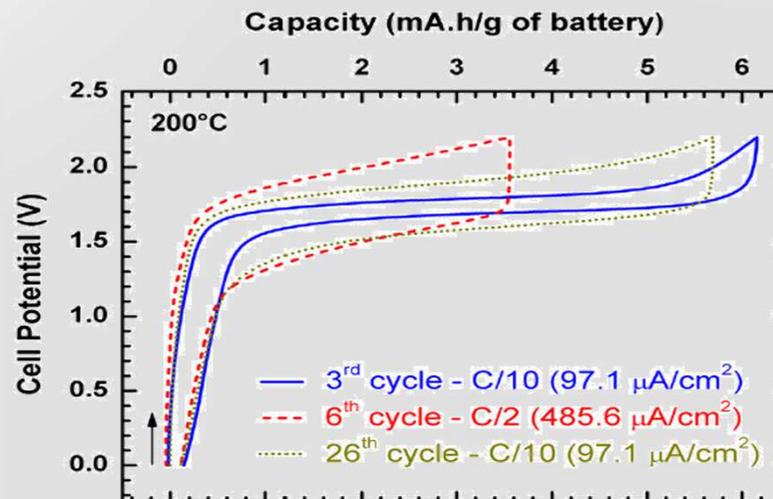
Composite electrode  
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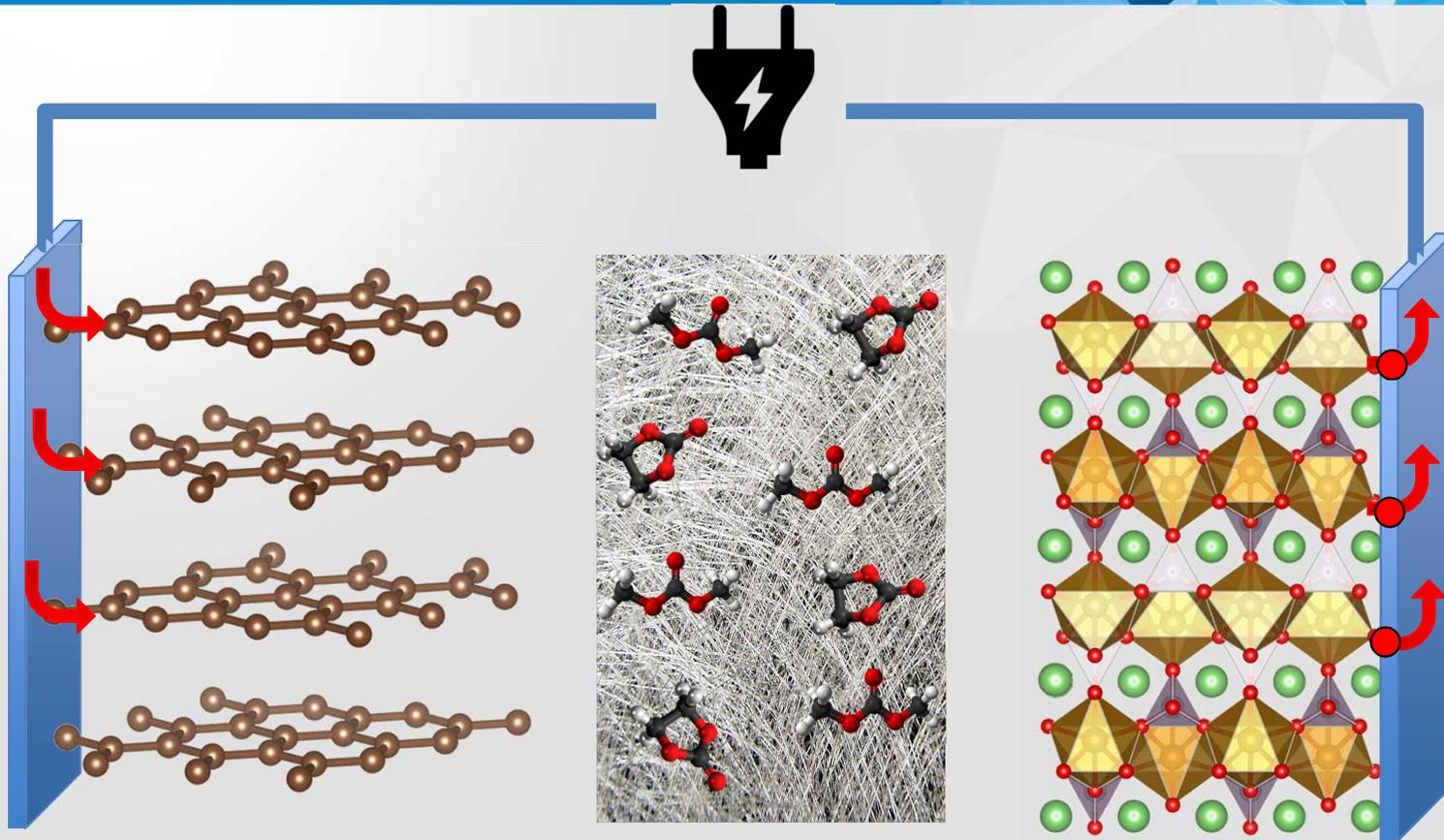
# ALL-NASICON Battery



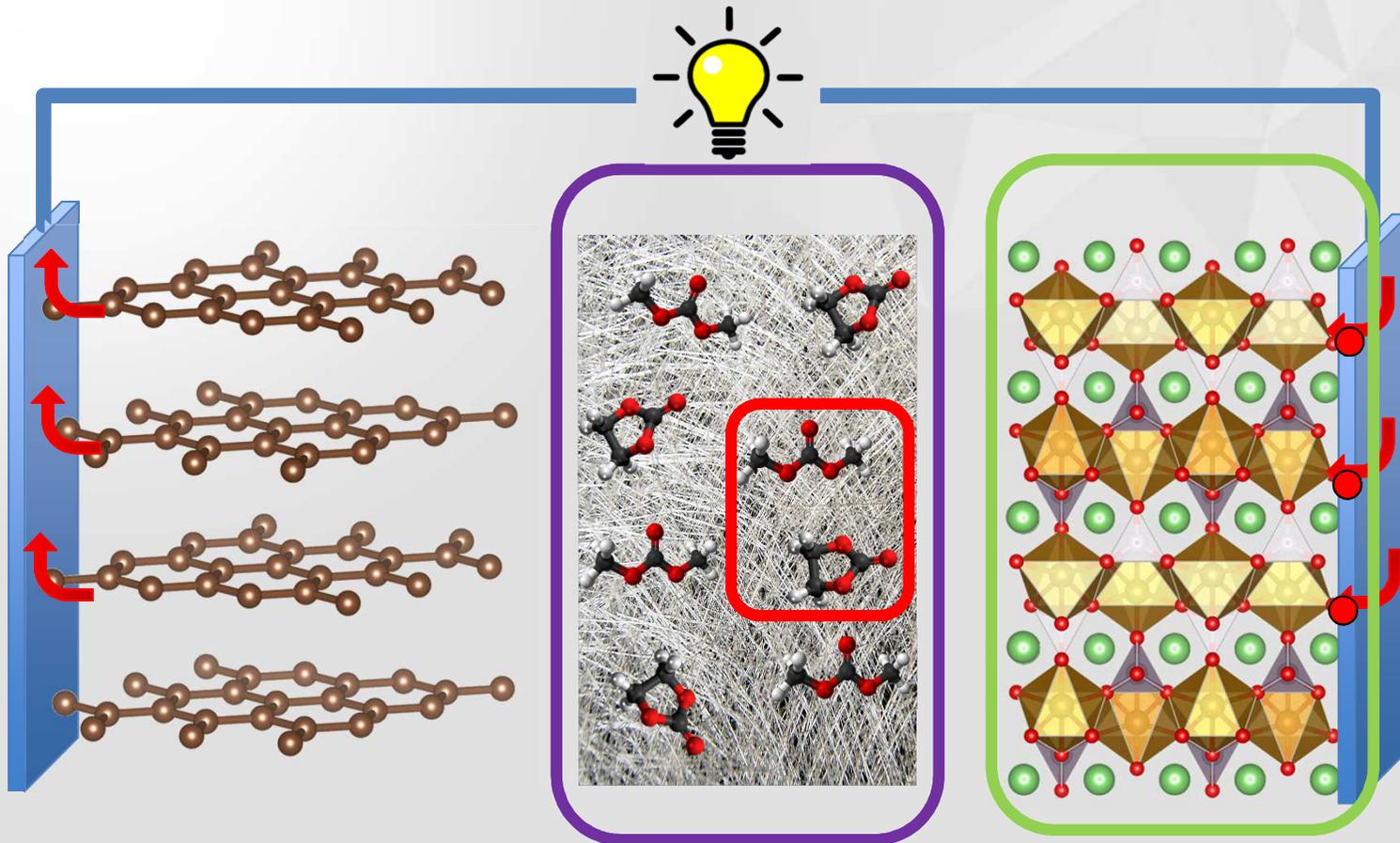
Electrochemical cell, can cycle up to 300°C !!!



# Li/Na-ion Battery : How does it work ?



# Li/Na-ion Battery : How does it work ?



# Diffraction in Real Time

## Lab X-Rays

XRD in the lab for In Situ and Ex-Situ studies

Application:  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

## Neutrons

- A new Electrochemical cell to study Li-ion battery materials

Application:  $\text{LiFePO}_4$

## Synchrotron X-Rays

High-angular resolution for battery materials

Application :  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

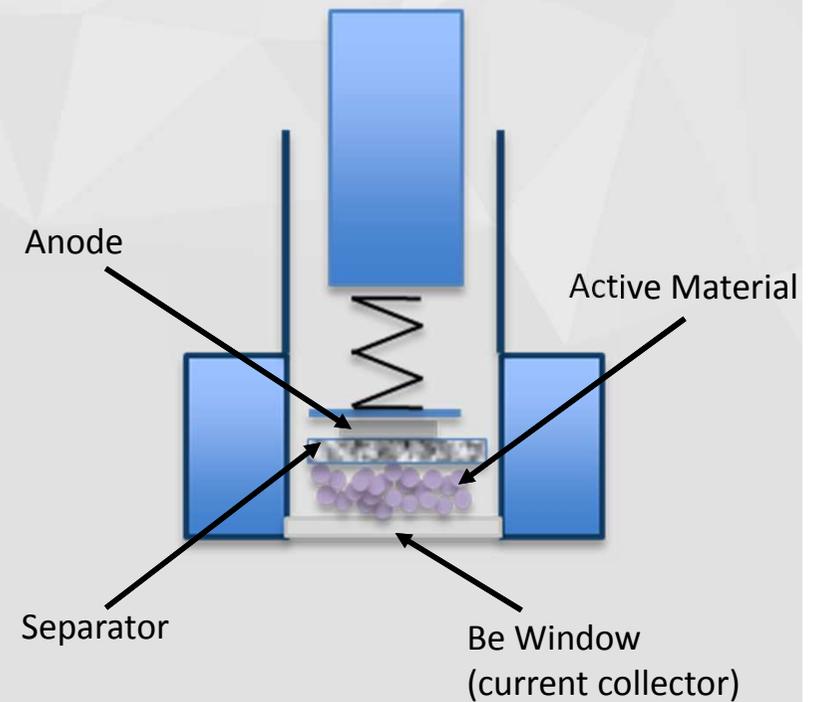
# Diffraction in Real Time

## Lab X-Rays

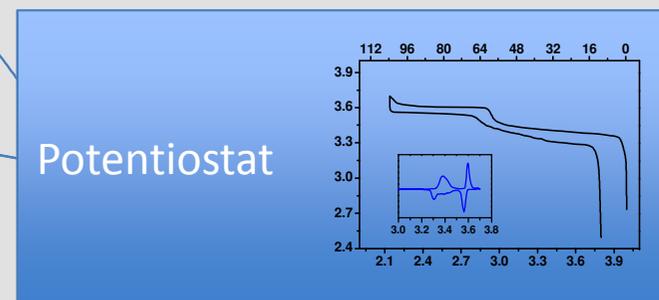
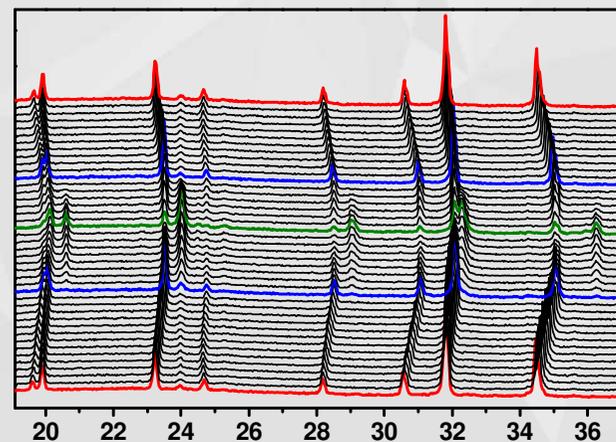
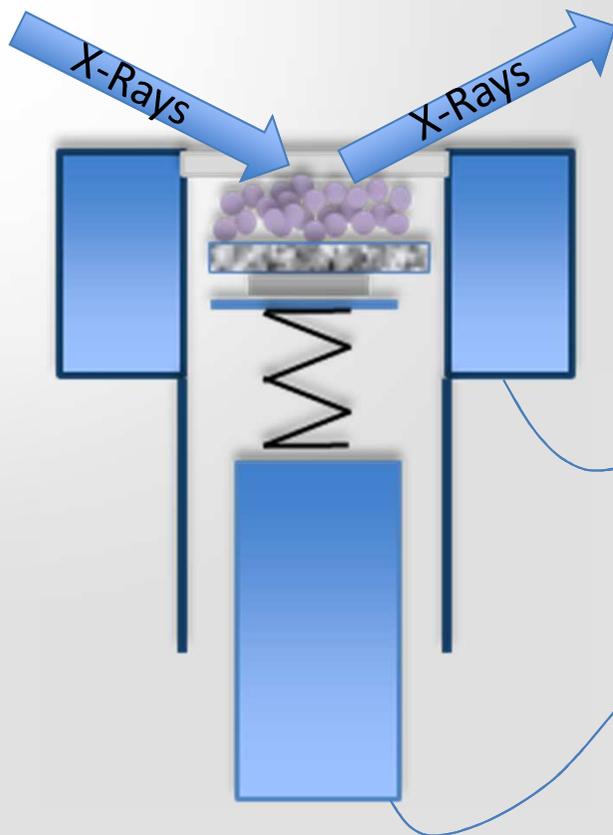
XRD in the lab for In Situ and Ex-Situ studies

Application:  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

# Challenge: Following the crystal structure changes upon cycling



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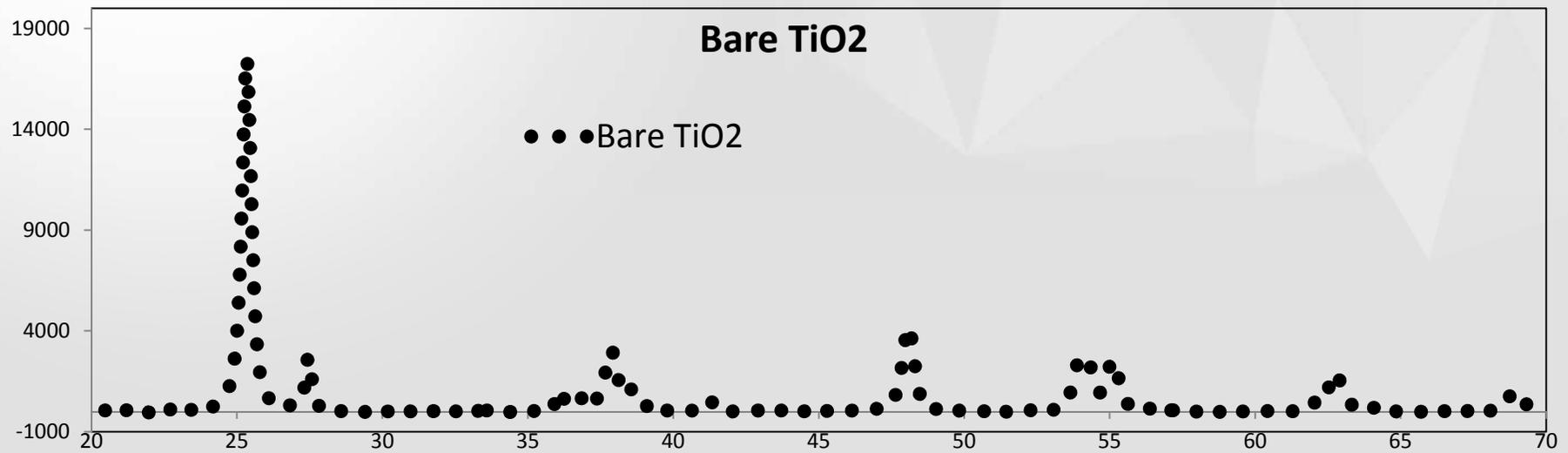
## How to mount the cell ?



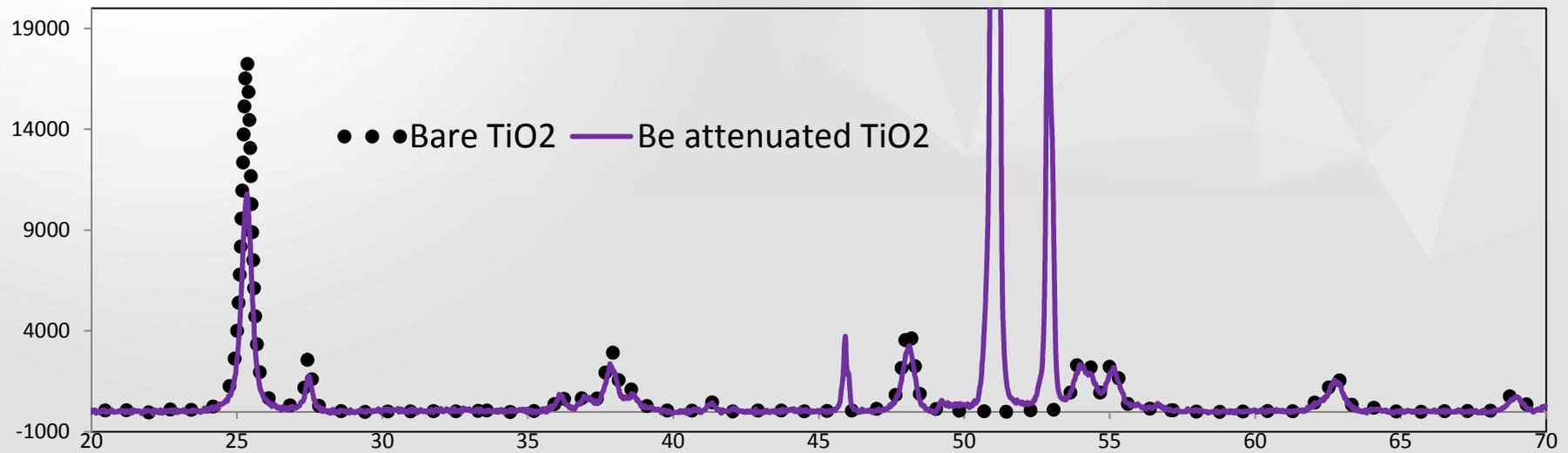
side view of the cell

# Intensity attenuation using Be window

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# Intensity attenuation using Be window

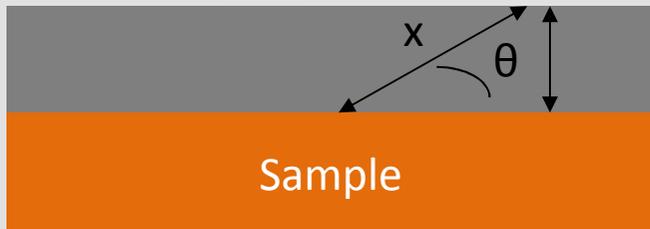


# Intensity attenuation using Be window

## Beer-Lambert law

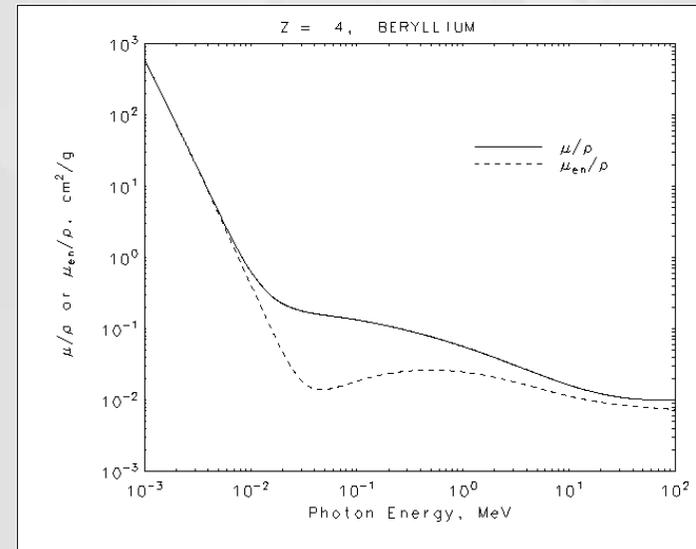
$$I = I_0 \cdot e^{-\mu \cdot x}$$

I: observed intensity  
 $I_0$ : initial intensity  
 $\mu$ : Mass Attenuation Coefficient  
x: thickness crossed



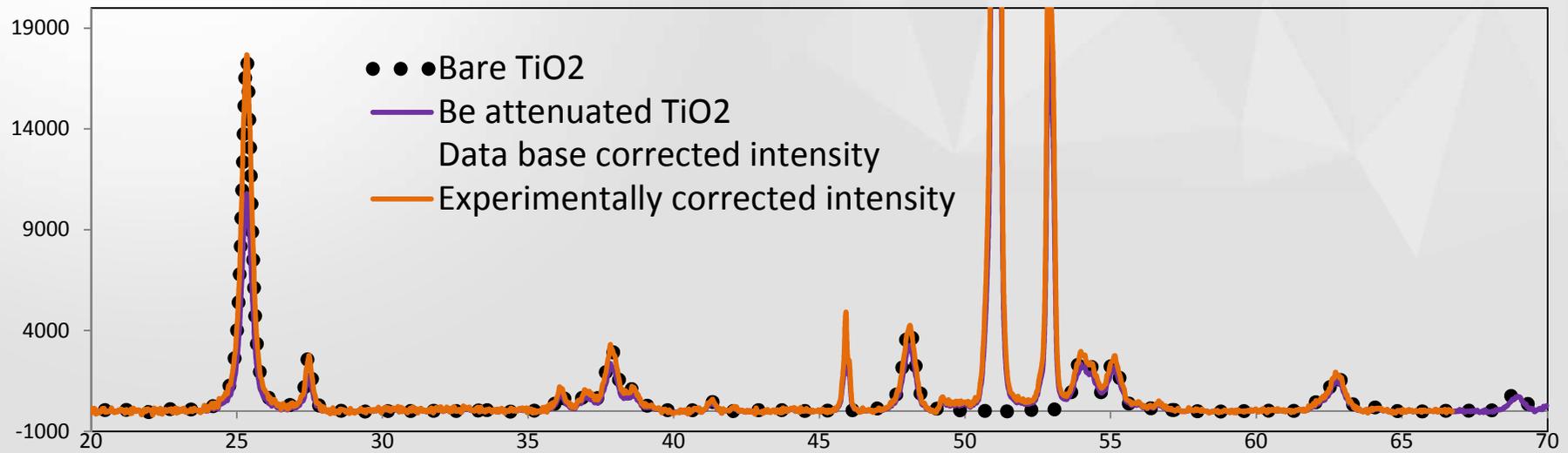
$$x = h / \sin(2\theta/2)$$

Source: NIST

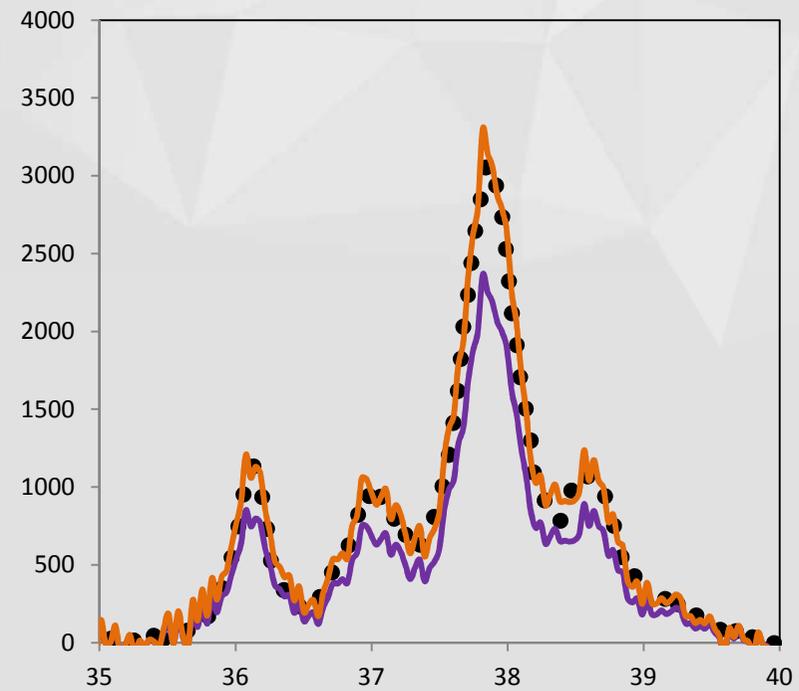
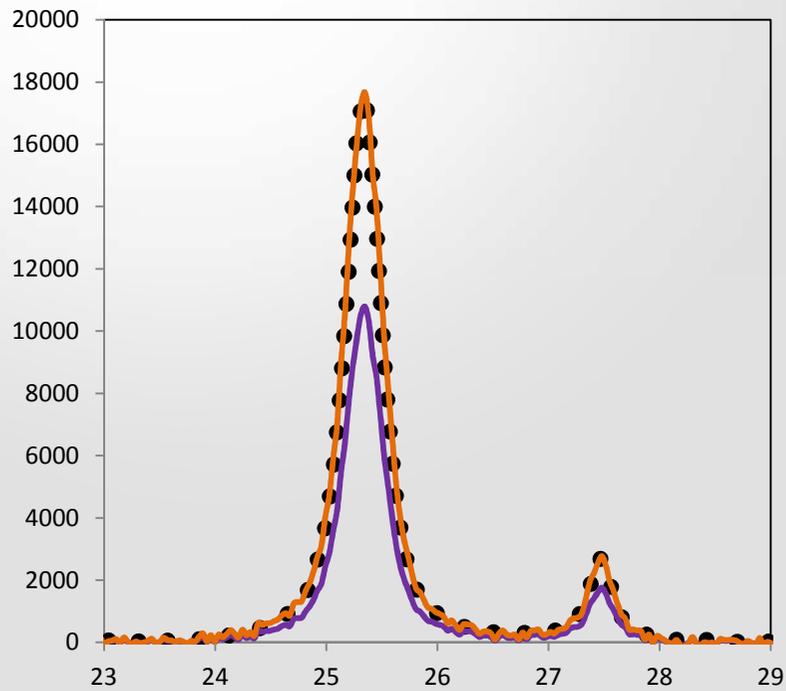


For  $\lambda_{Cu, \alpha 1}$   $\mu = 1.61 \text{ cm}^{-1}$

# Intensity attenuation using Be window

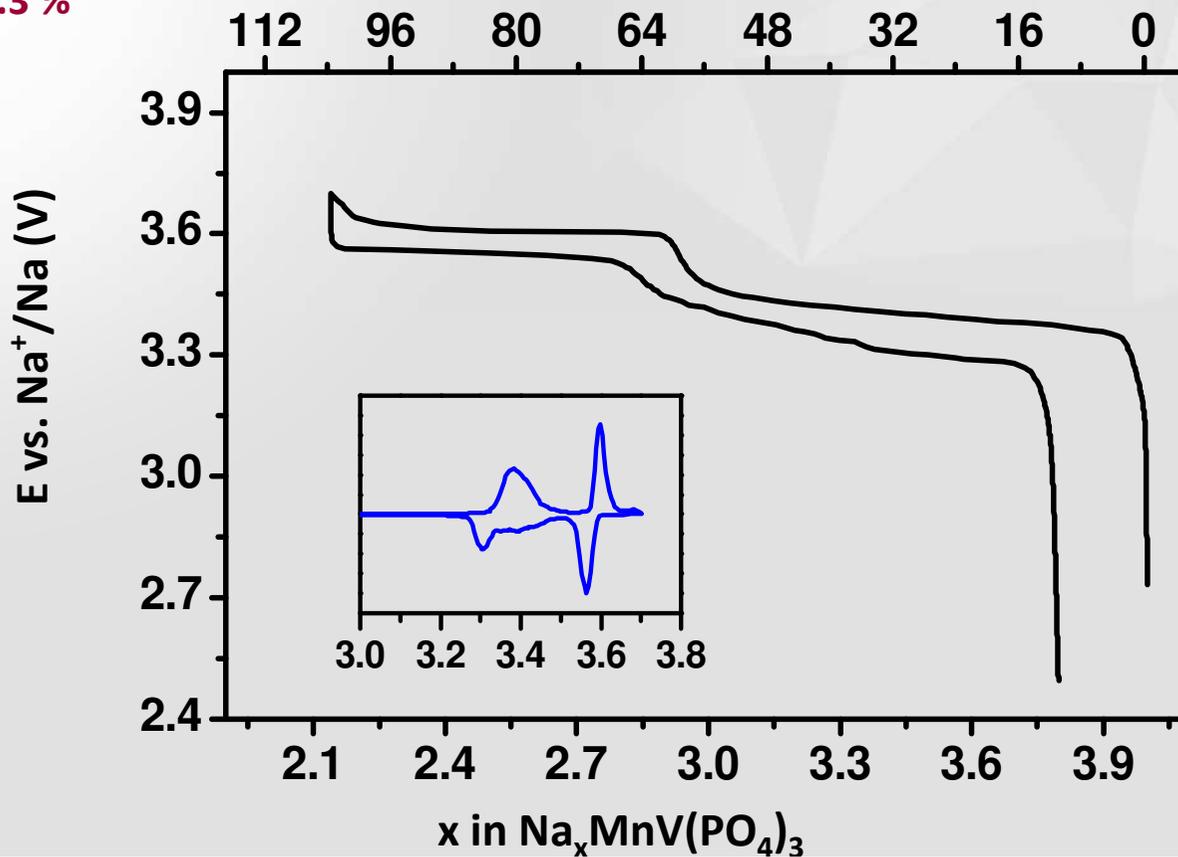


# Intensity attenuation using Be window

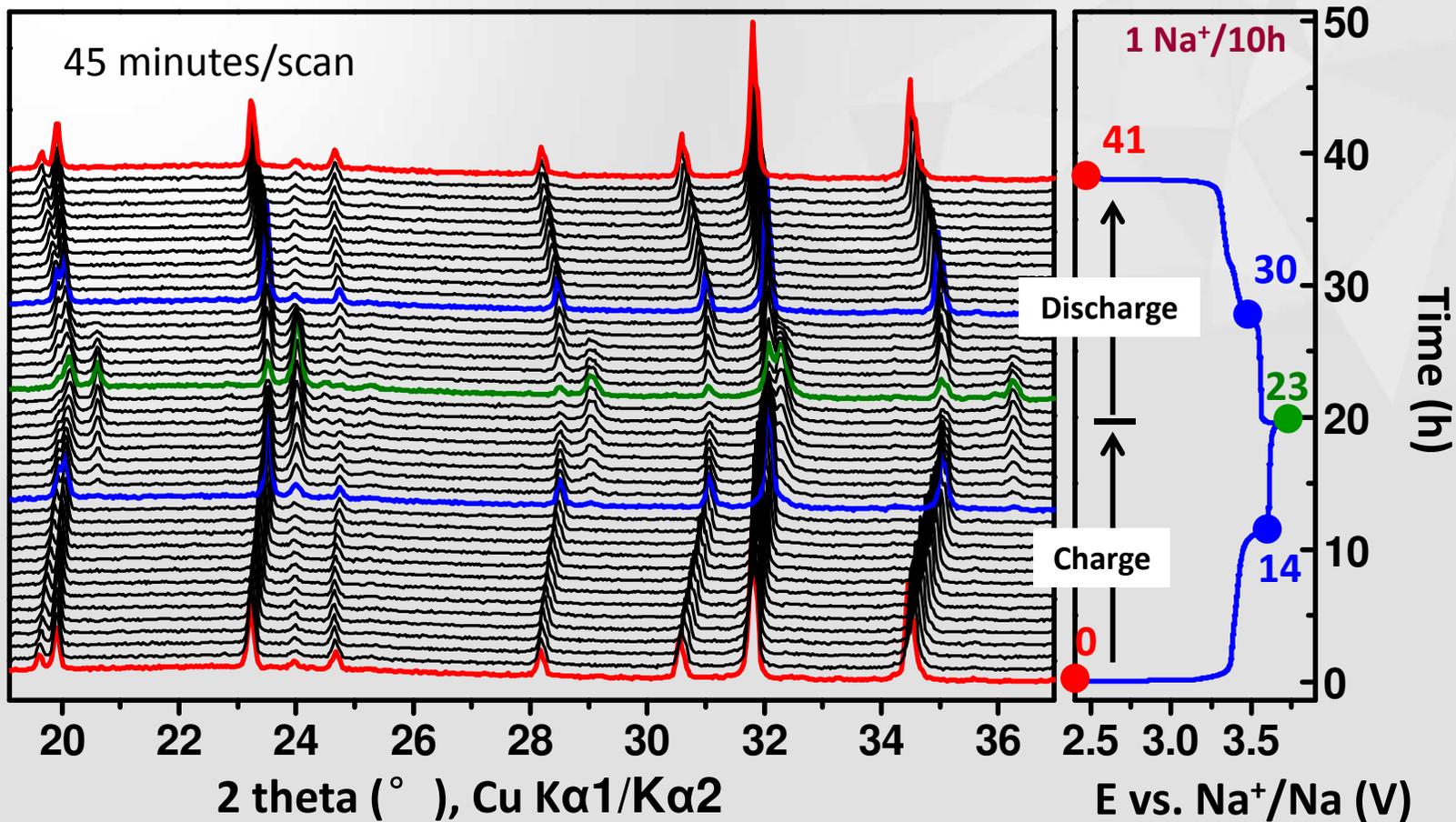


# Operando Measurements using Lab X-rays: The example of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

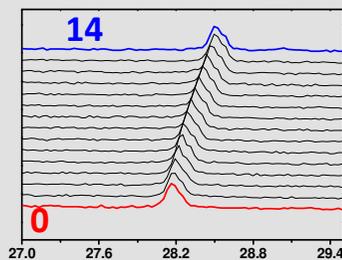
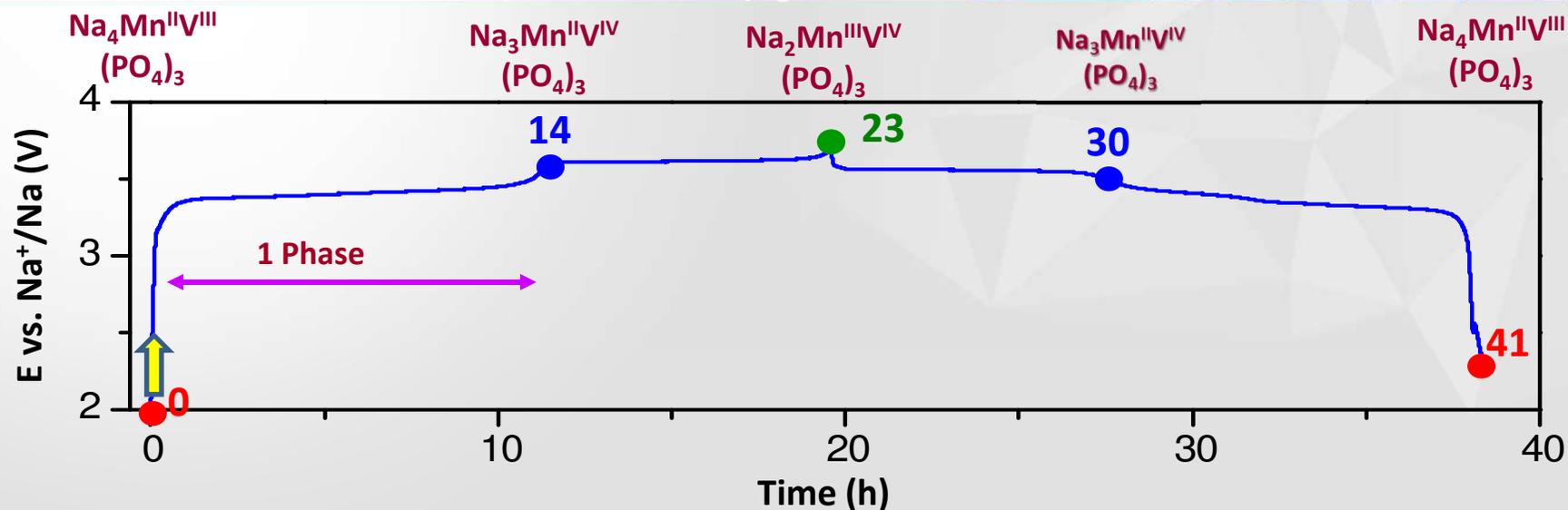
1  $\text{Na}^+$ /20h,  $w_{\text{AM}} = 83.3\%$



# Operando Measurements using Lab X-rays: The example of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

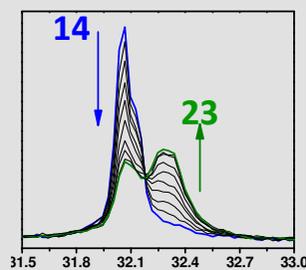
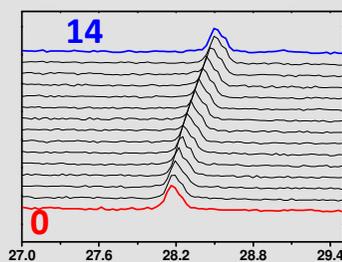
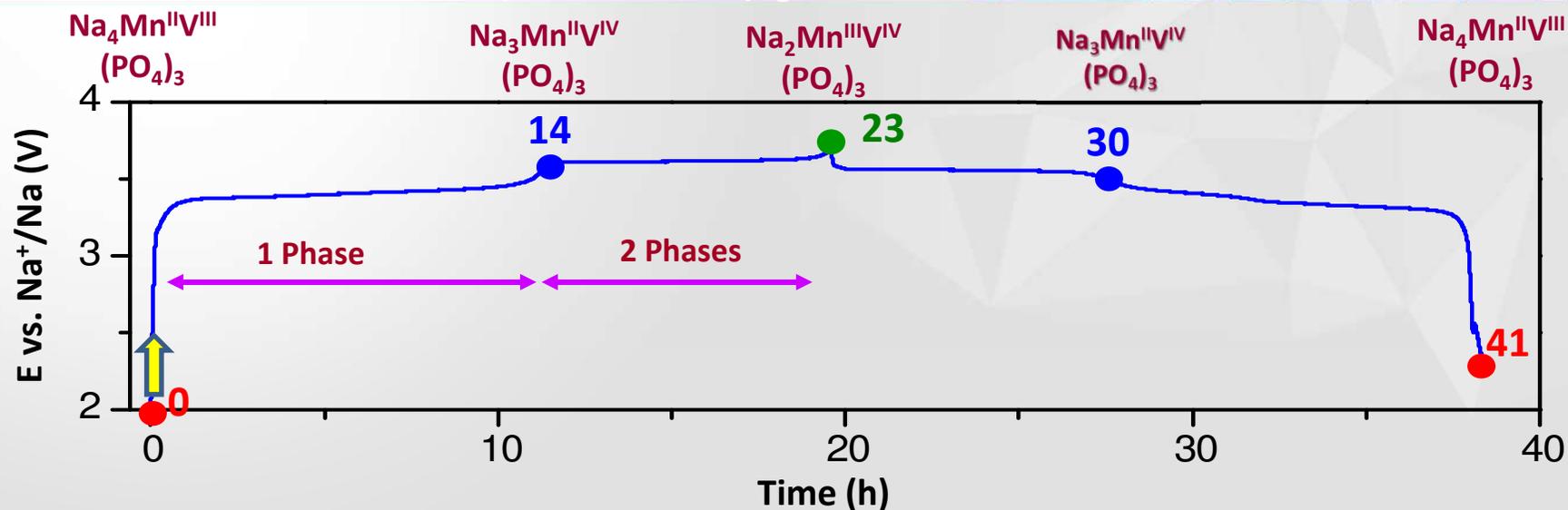


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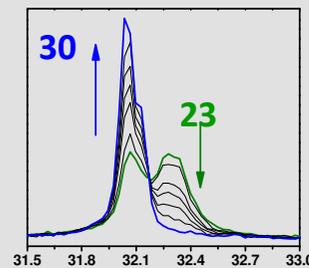
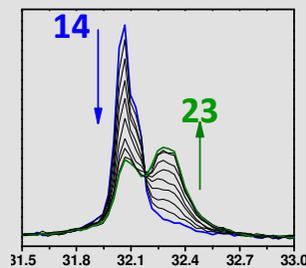
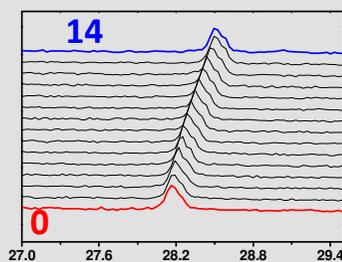
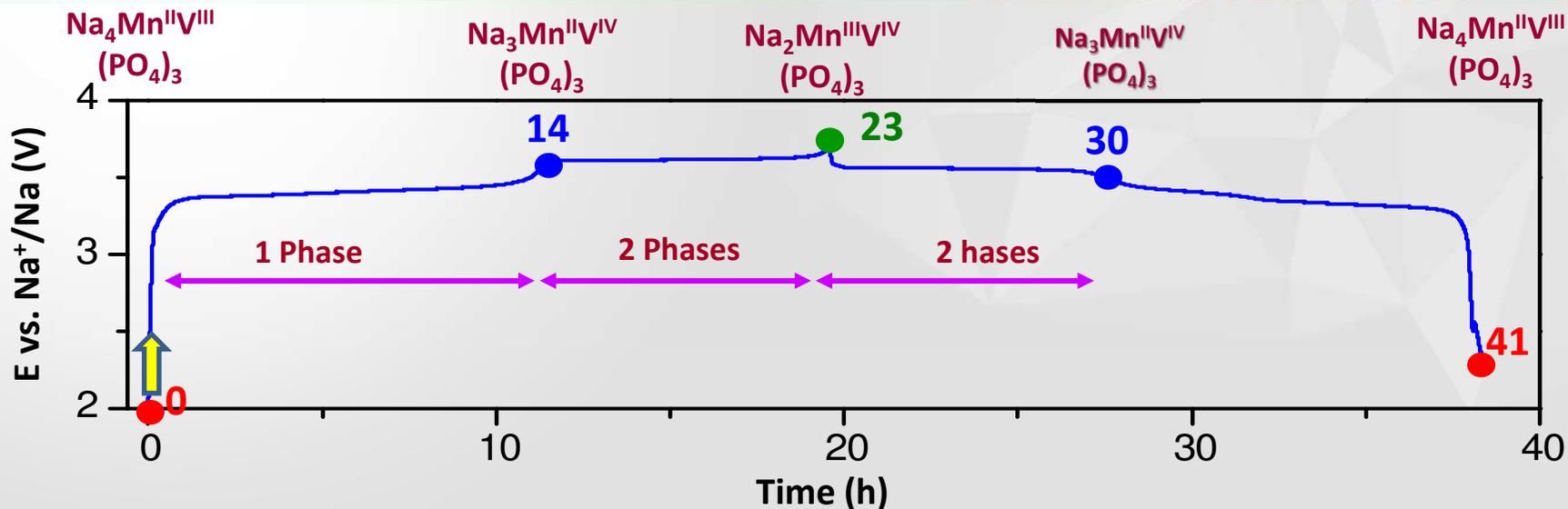
2 theta (°), Cu  $\text{K}\alpha_1/\text{K}\alpha_2$

# Operando Measurements using Lab X-rays: The example of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$



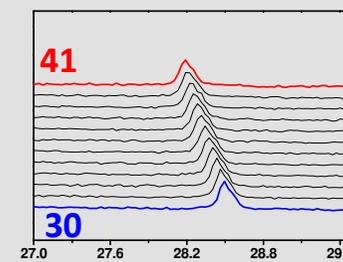
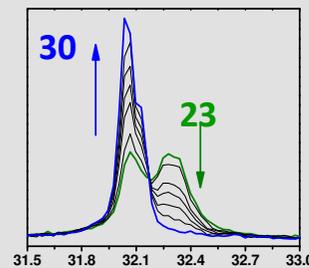
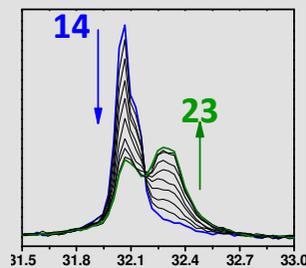
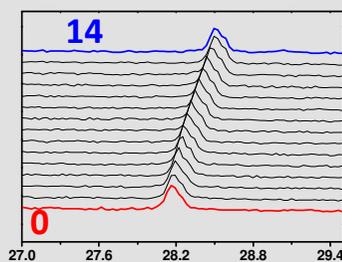
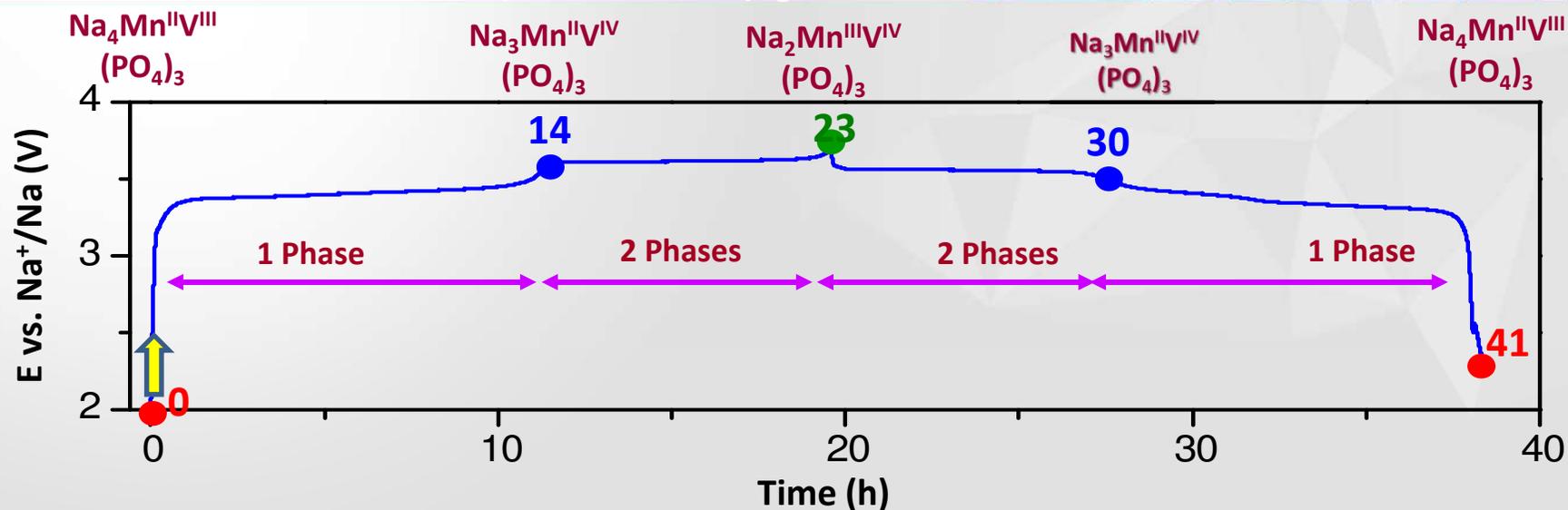
$2\theta$  (°), Cu  $\text{K}\alpha_1/\text{K}\alpha_2$

# Operando Measurements using Lab X-rays: The example of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$



2 theta (°), Cu  $\text{K}\alpha_1/\text{K}\alpha_2$

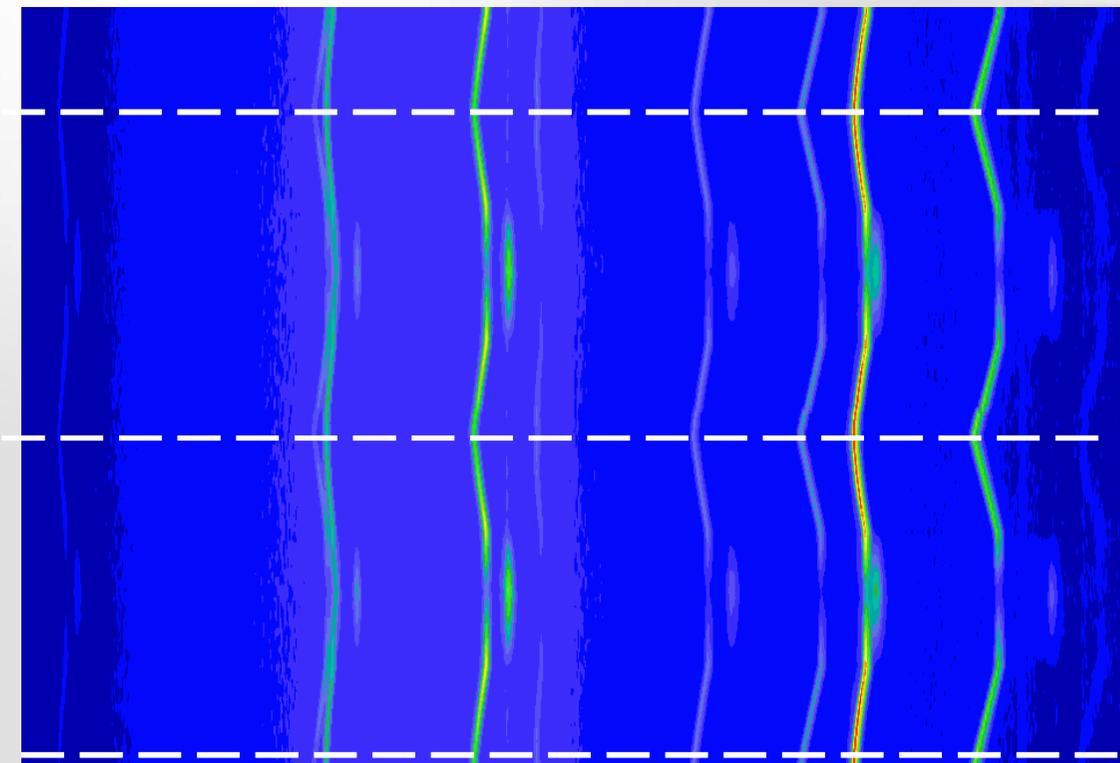
# Operando Measurements using Lab X-rays: The example of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$



2 theta (°), Cu K $\alpha$ 1/K $\alpha$ 2

# Operando Measurements using Lab X-rays: The example of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

Very high reversibility



# Diffraction in Real Time

## Lab X-Rays

XRD in the lab for In Situ and Ex-Situ studies

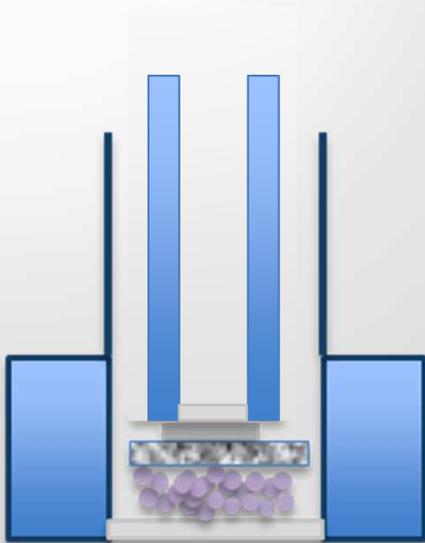
Application:  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

## Synchrotron X-Rays

High-angular resolution for battery materials

Application :  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

# Operando Measurements using Synchrotron X-rays



J.B. Leriche et al., JES, 2010



A606

*Journal of The Electrochemical Society*, 157 (5) A606-A610 (2010)  
0013-4651/2010/157(5)/A606/\$528.00 © The Electrochemical Society



## An Electrochemical Cell for *Operando* Study of Lithium Batteries Using Synchrotron Radiation

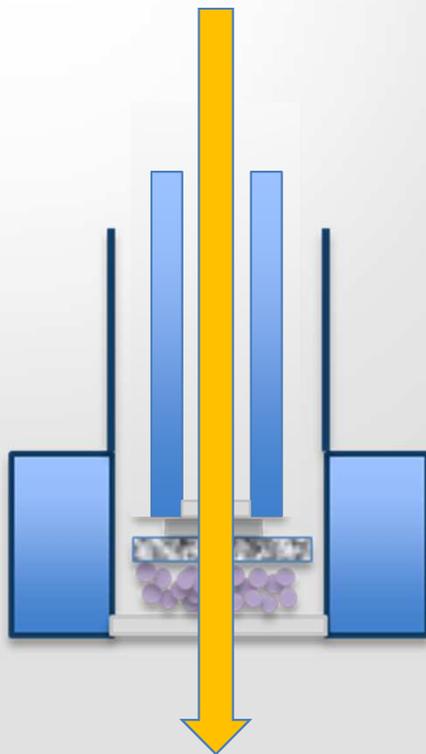
J. B. Leriche,<sup>a</sup> S. Hamelet,<sup>a</sup> J. Shu,<sup>a</sup> M. Morcrette,<sup>a</sup> C. Masquelier,<sup>a,z</sup>  
G. Ouvrard,<sup>b</sup> M. Zerrouki,<sup>a</sup> P. Soudan,<sup>b</sup> S. Belin,<sup>c</sup> E. Elkaim,<sup>c</sup> and F. Baudalet<sup>d</sup>

<sup>a</sup>Laboratoire de Réactivité et de Chimie des Solides, Université de Picardie Jules Verne, CNRS UMR 6007, 80039 Amiens Cedex 9, France

<sup>b</sup>Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS UMR 6502, BP 32229, 44322 Nantes Cedex 3, France

<sup>c</sup>Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin BP 48, 91192 Gif sur Yvette, France

# Operando Measurements using Synchrotron X-rays



J.B. Leriche et al., JES, 2010



A606

*Journal of The Electrochemical Society*, 157 (5) A606-A610 (2010)  
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## An Electrochemical Cell for *Operando* Study of Lithium Batteries Using Synchrotron Radiation

J. B. Leriche,<sup>a</sup> S. Hamelet,<sup>a</sup> J. Shu,<sup>a</sup> M. Morcrette,<sup>a</sup> C. Masquelier,<sup>a,z</sup>  
G. Ouvrard,<sup>b</sup> M. Zerrouki,<sup>a</sup> P. Soudan,<sup>b</sup> S. Belin,<sup>c</sup> E. Elkaim,<sup>c</sup> and F. Baudalet<sup>d</sup>

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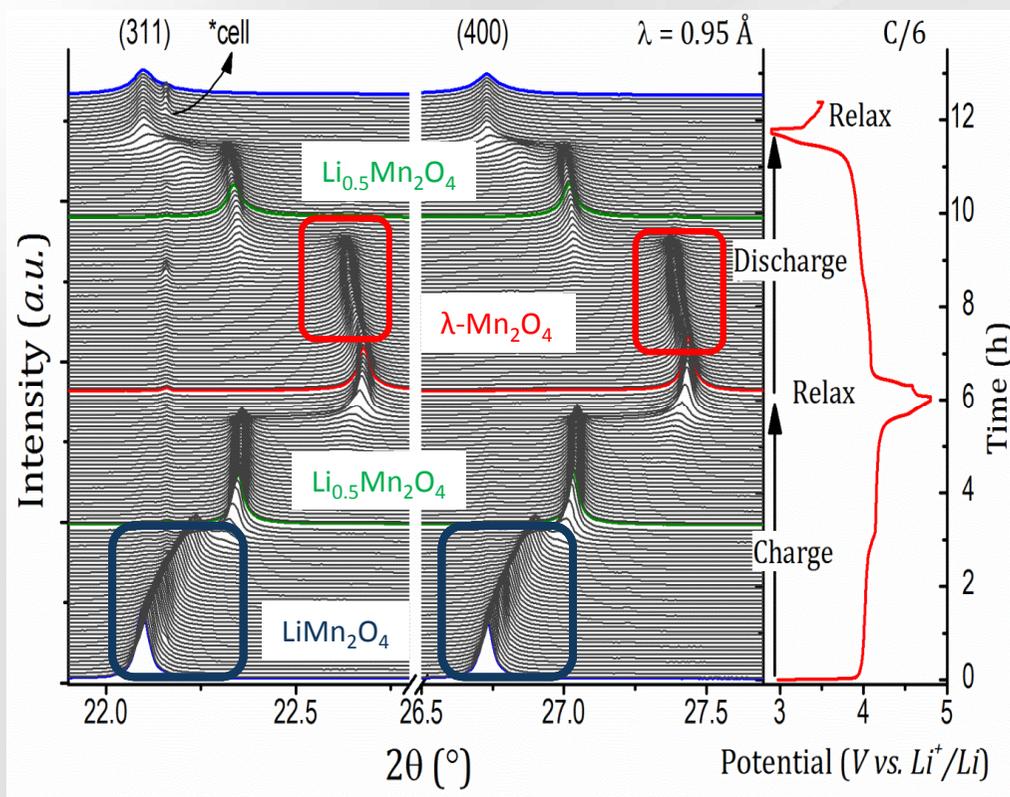
<sup>c</sup>Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin BP 48, 91192 Gif sur Yvette, France

# Charge Ordering in $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$



Operando synchrotron XRD, ALBA, Barcelona

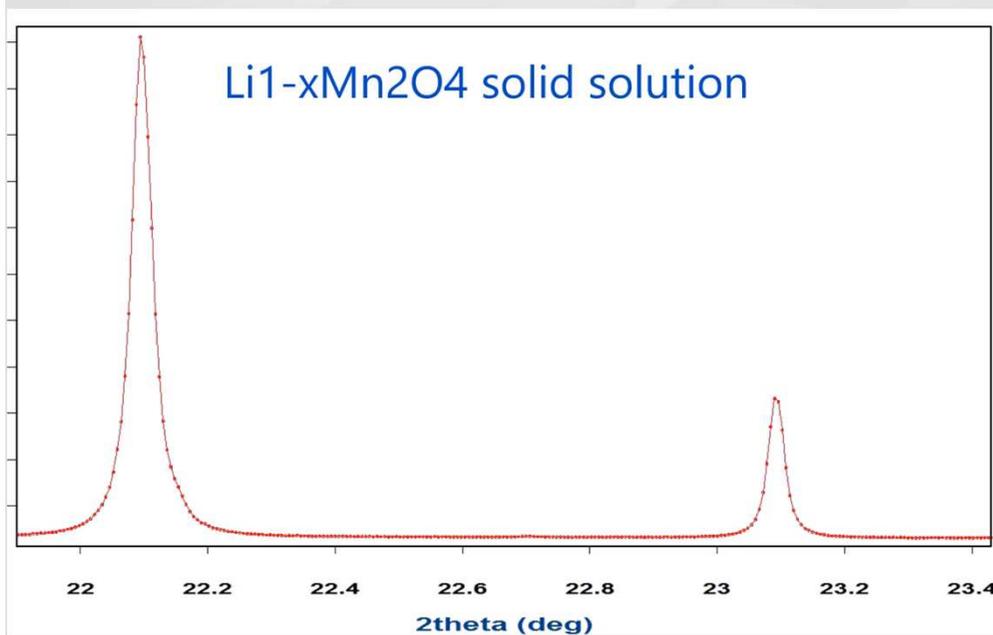
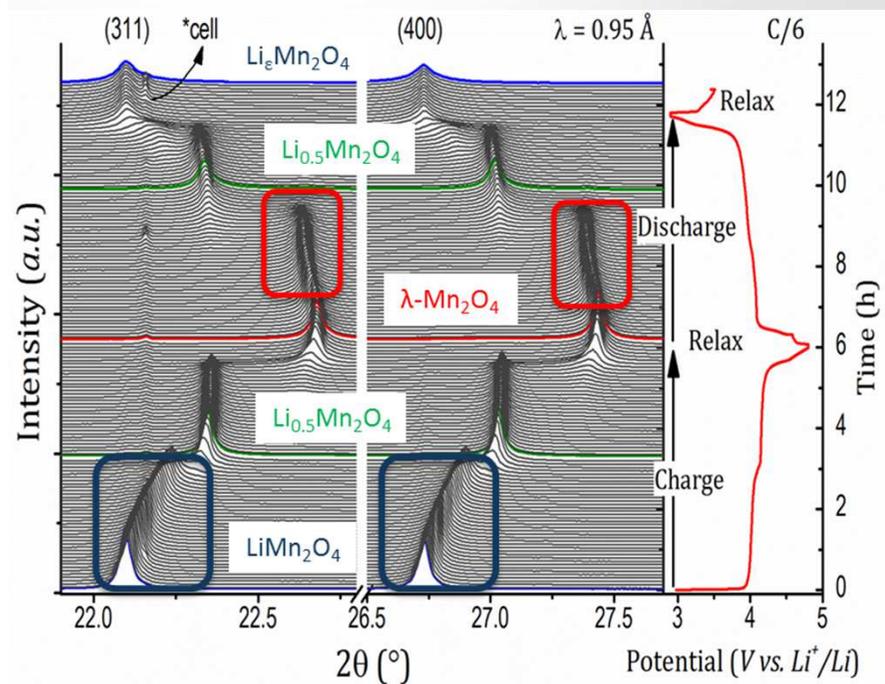
Few secondes /scan



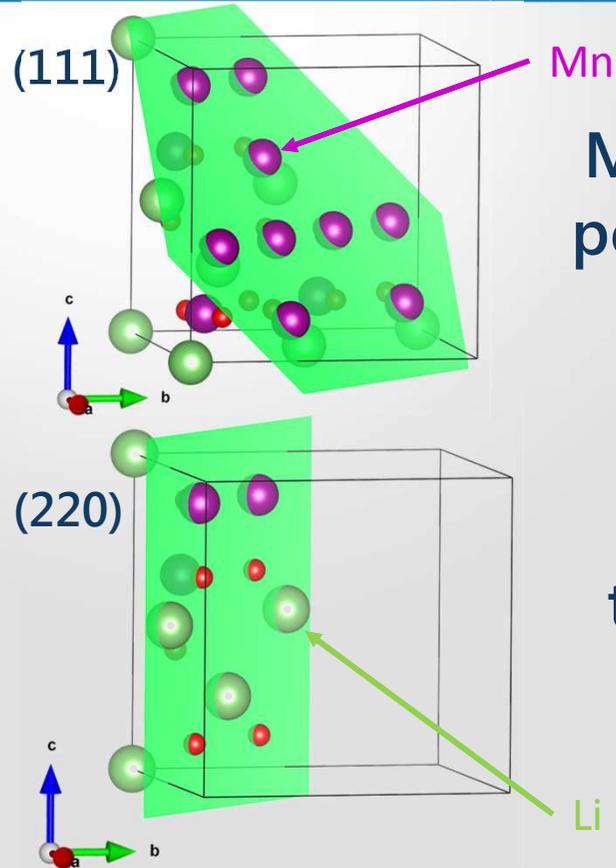
M. Bianchini, et al, *Acta Cryst.*, B71, 688-701, 2015

# Charge Ordering in $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

Operando synchrotron XRD, ALBA, Barcelona

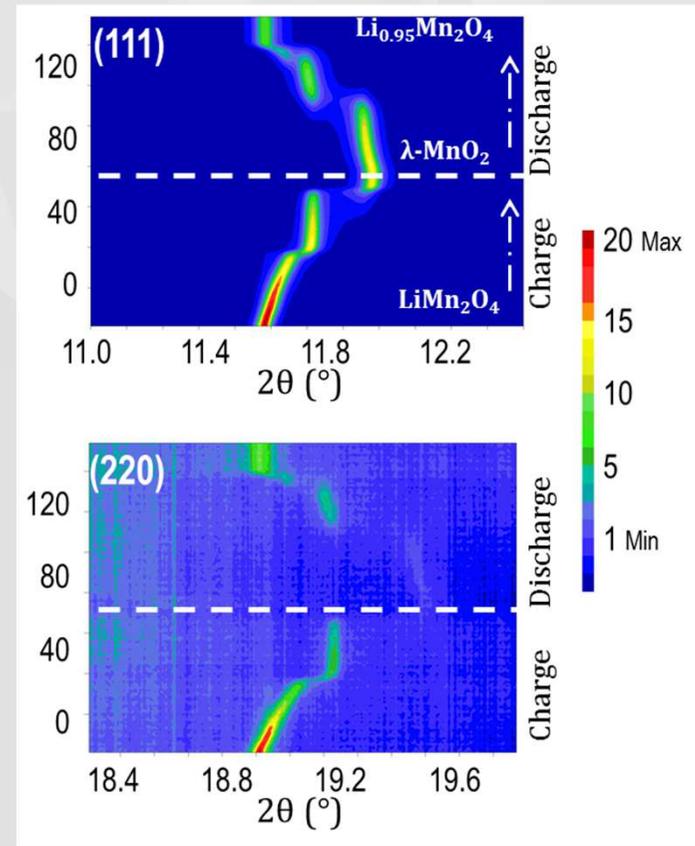


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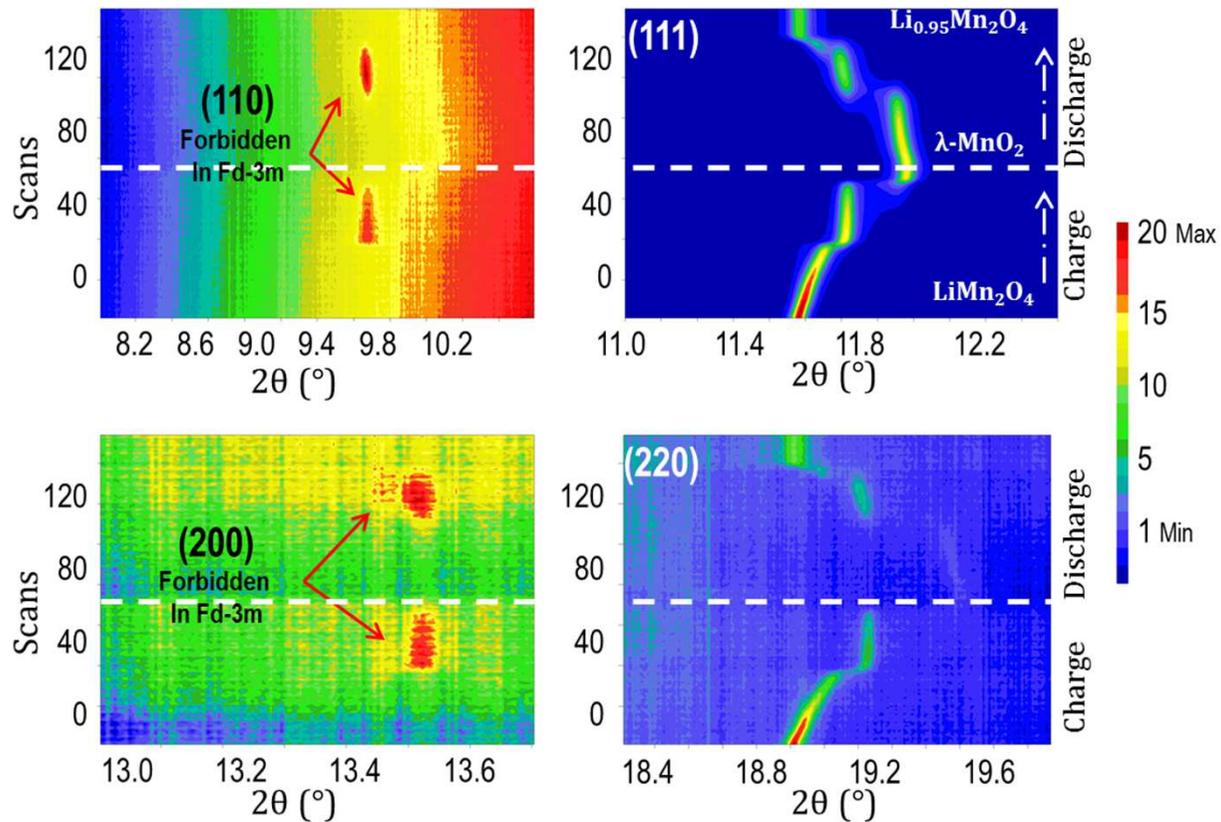


Most intense peak in spinel

Correlated to atoms in 8a site : Li

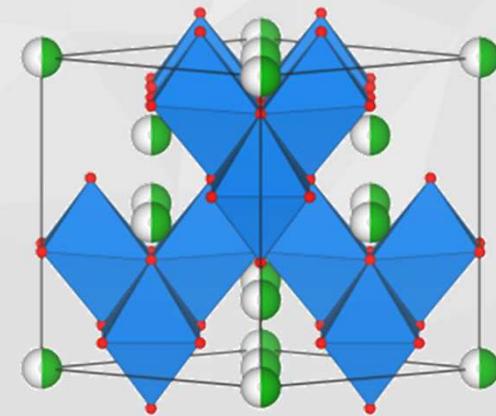
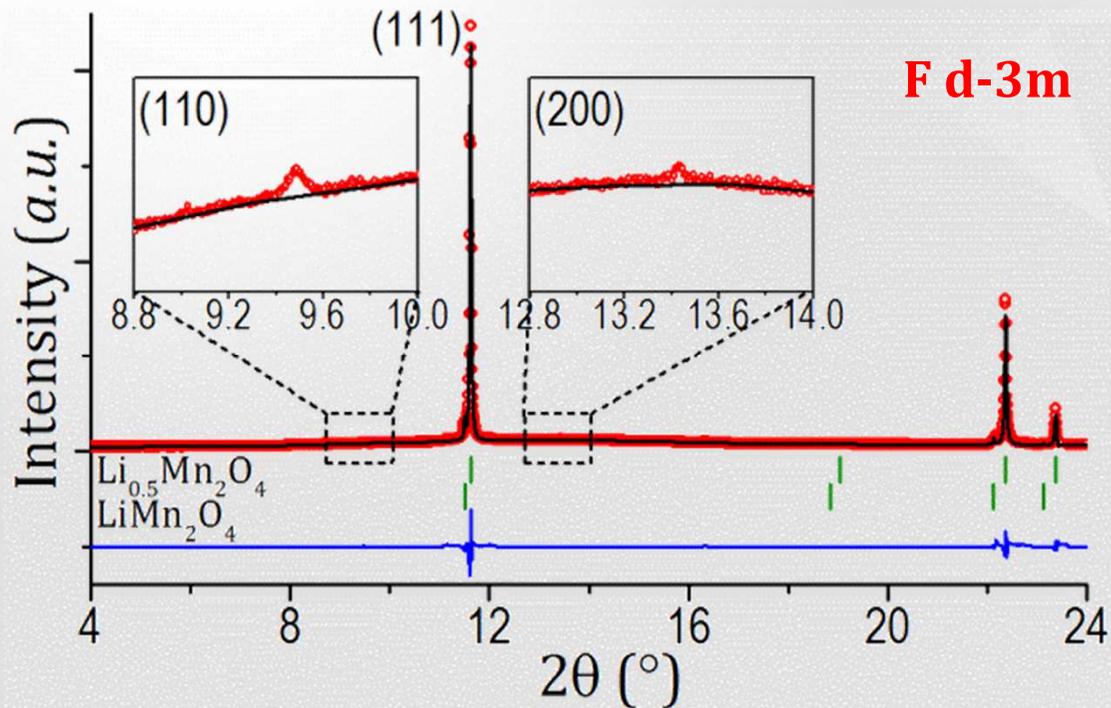


# Charge Ordering in $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$



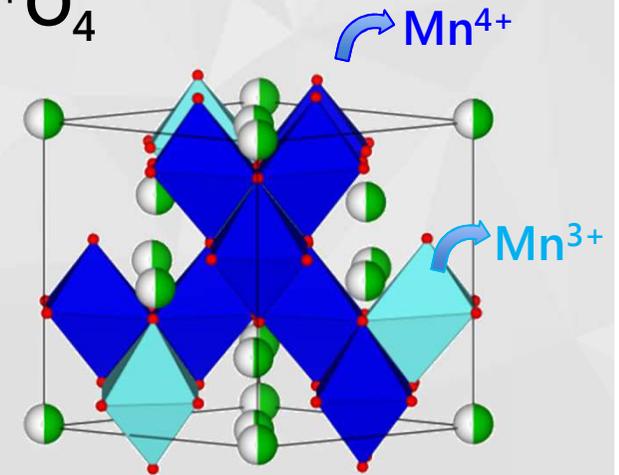
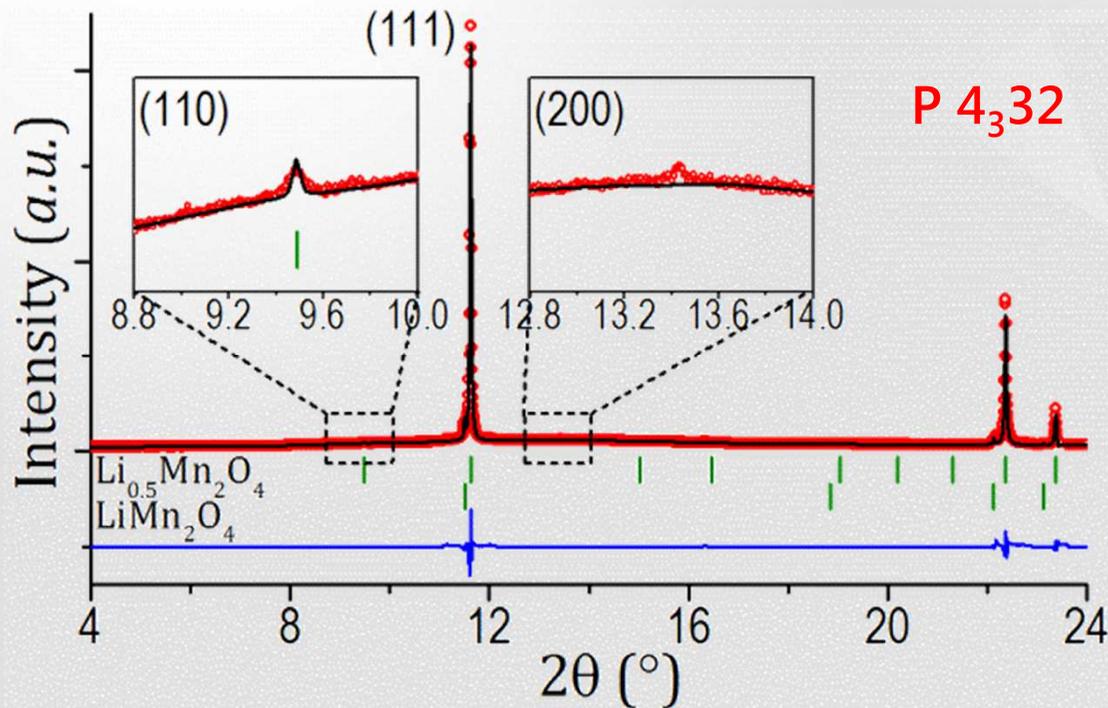
# Charge Ordering in $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

$\text{Li}_{0.5}\text{Mn}_2\text{O}_4 \ll \text{Mn}^{3.75+} \gg$



Disordered  $\text{Mn}^{3+}/\text{Mn}^{4+}$  cations  
Lithium in  $8a$  position, SOF =  $\frac{1}{2}$

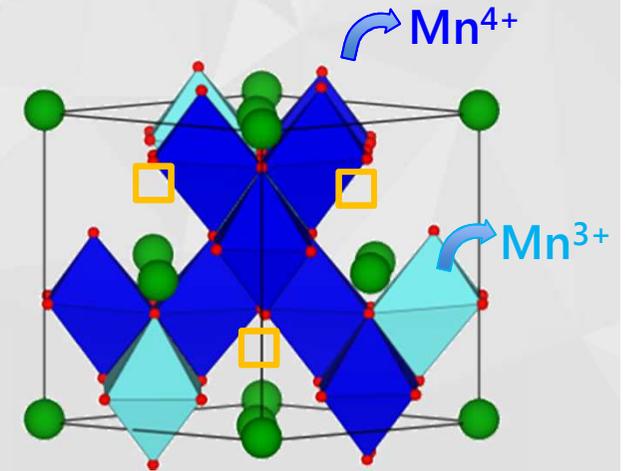
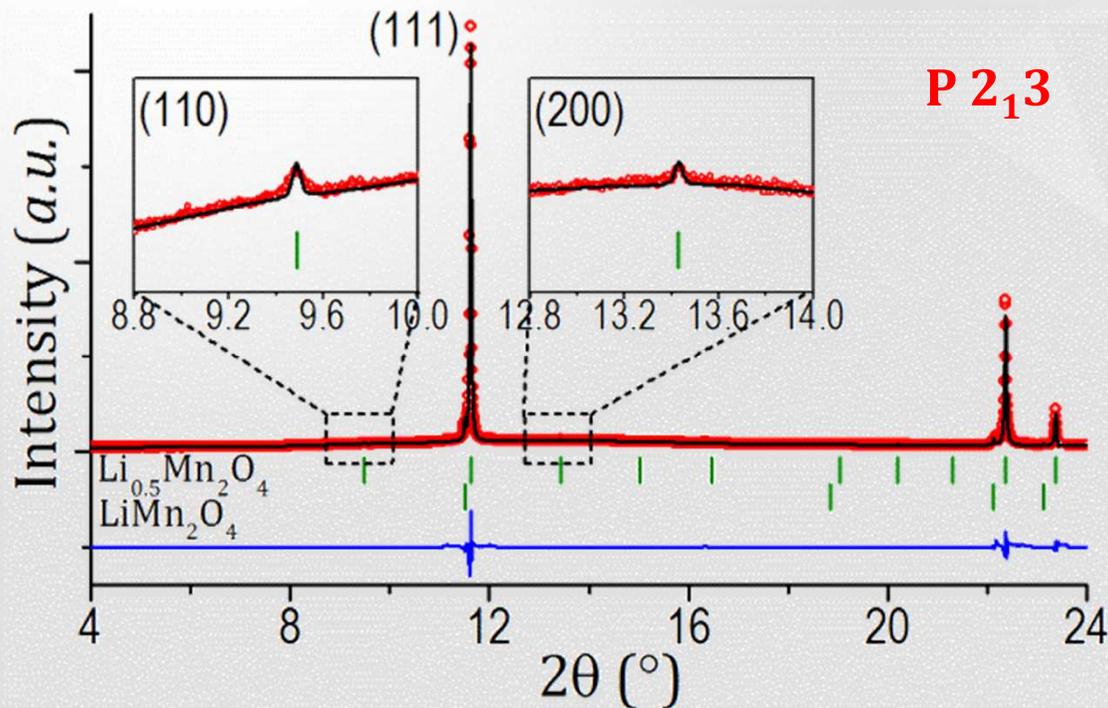
# Charge Ordering in $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$



**Ordered** 1:3 Mn<sup>3+</sup>/Mn<sup>4+</sup> (Mn<sup>3.75+</sup>)  
 Lithium in  $\delta a$  position, SOF =  $\frac{1}{2}$   
 Similar to  $\text{LiNi}_{0.5}^{2+}\text{Mn}_{1.5}^{4+}\text{O}_4$

# Charge & Li Ordering in $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

$\text{Li}_{0.5}\text{Mn}_2\text{O}_4 \ll \text{Mn}^{3.75+} \gg$



Ordered 1:3  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ( $\text{Mn}^{3.75+}$ )  
Lithium in fully occupied 4a position

# Diffraction in Real Time

## Lab X-Rays

XRD in the lab for In Situ and Ex-Situ studies

Application:  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$

## Neutrons

- A new Electrochemical cell to study Li-ion battery materials

Application:  $\text{LiFePO}_4$

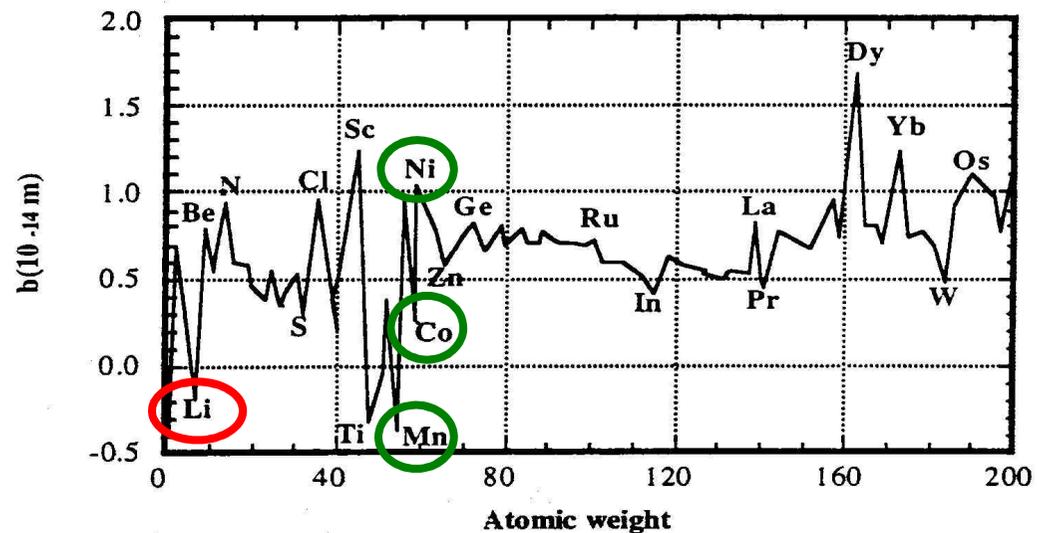
## Synchrotron X-Rays

High-angular resolution for battery materials

Application :  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

# Neutrons : pros...

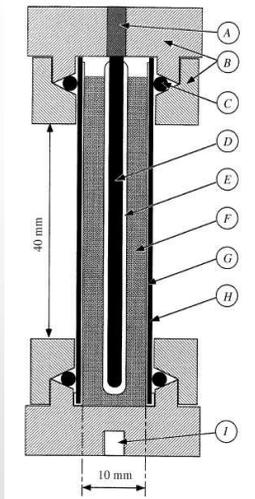
- **Neutrons' sensitivity to Lithium!**
- Neutrons' contrast between neighbouring elements
- Neutrons probe the whole electrode



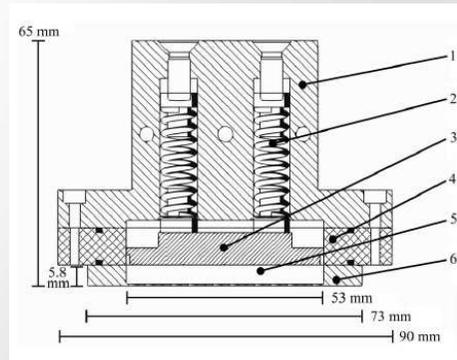
## ... and cons

- ▶ Availability
- ▶ Powder quantity ~200 mg
- ▶ Hydrogen incoherent scattering (replaced by deuterium)

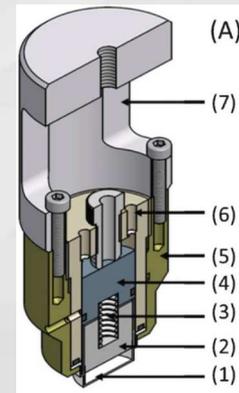
# Neutrons in-situ cells : a growing interest



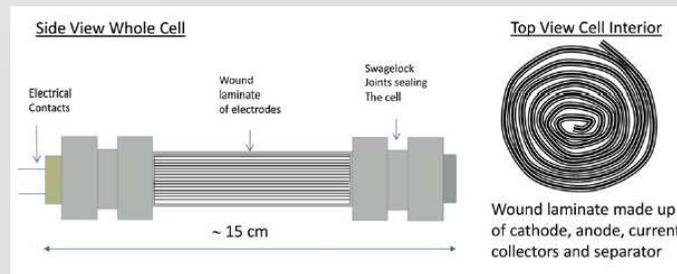
Bergstrom et al.,  
J. Appl. Cryst, 1998



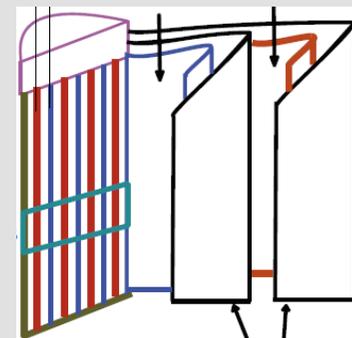
Rosciano et al.,  
J. Appl. Cryst, 2008



Godbole et al.,  
RSC advances, 2013

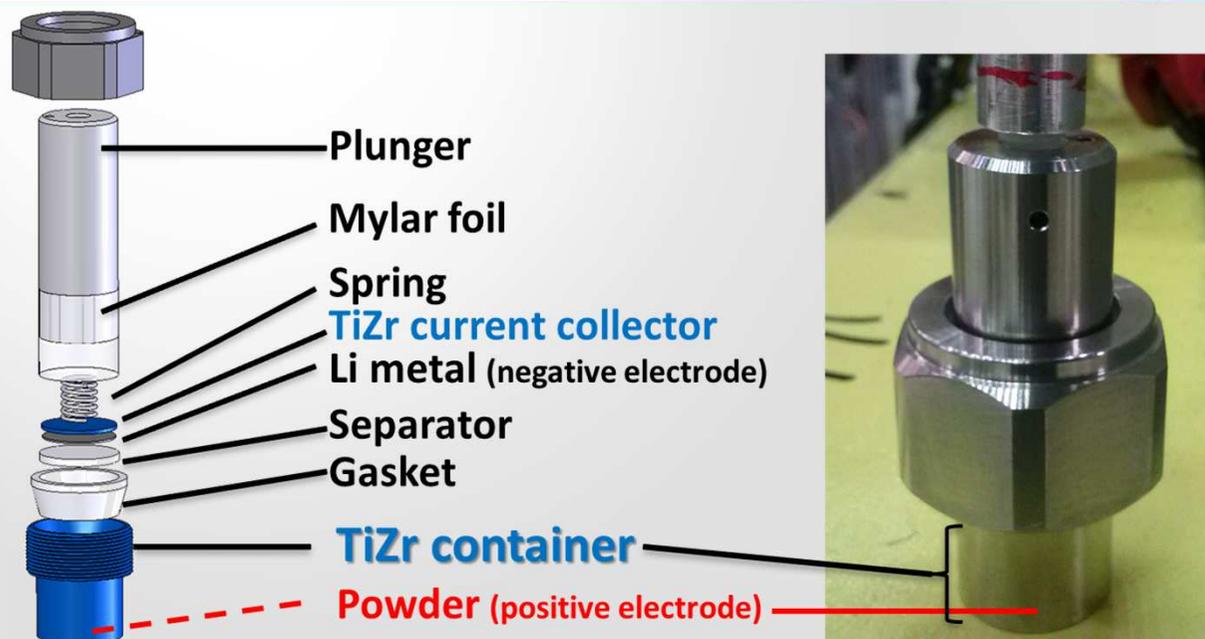


Roberts et al.,  
J. Power Sources, 2012



Sharma et al., S.  
State Ionics, 2011

# A new electrochemical cell for in-situ NPD



## Positive electrode:

- 80 wt% Active Material
- 10 wt% Csp
- 10 wt% Binder  $C_2F_4$

Total mass = 200 mg

## Electrolyte:

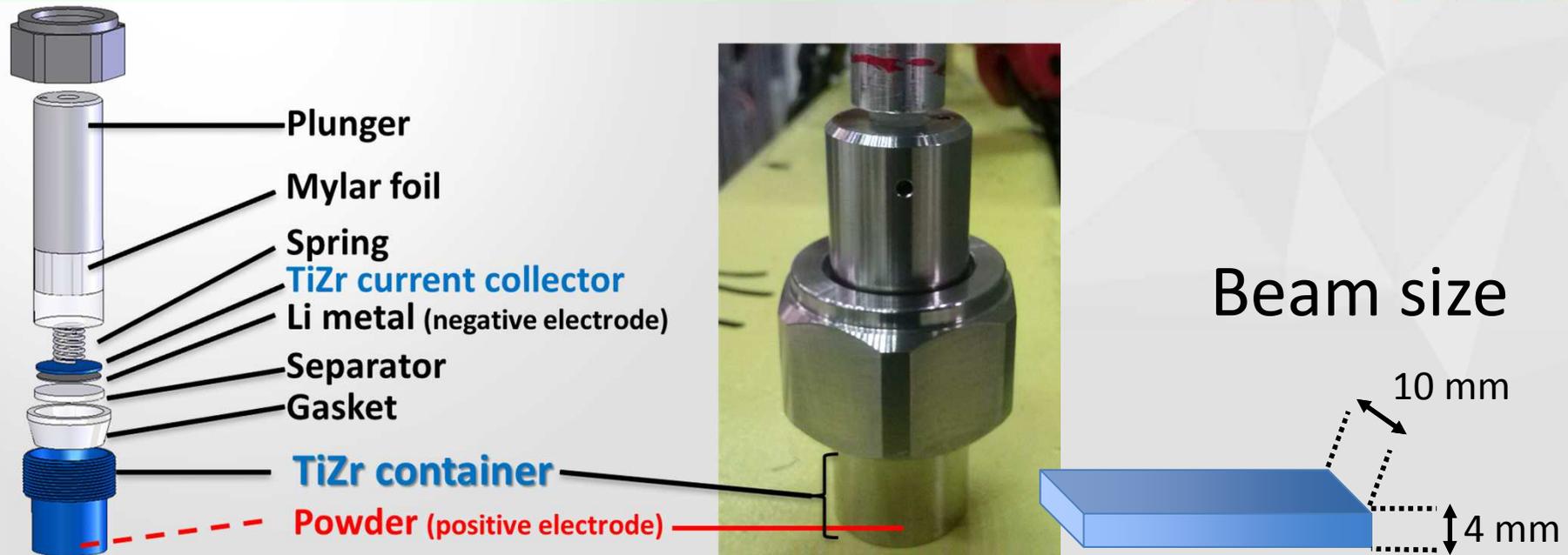
- $LiPF_6$  in deuterated EC/DMC

## Separator

- $SiO_2$  glass fiber

# NO HYDROGEN

# A new electrochemical cell for in-situ NPD



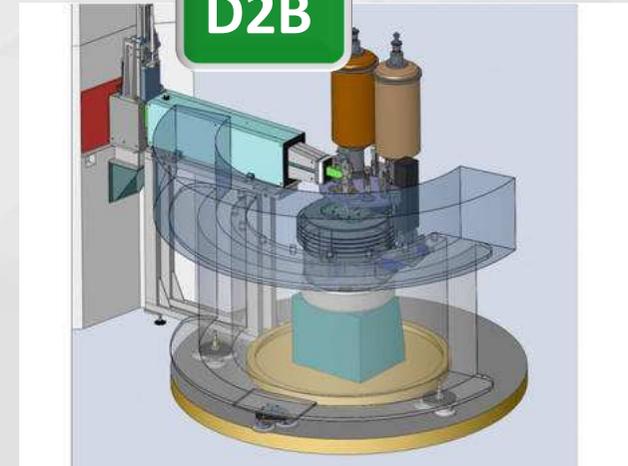
# A new electrochemical cell for in-situ NPD

D20



High intensity neutron flux  
1 pattern=10 minutes  
For Rietveld → 3 or 6 patterns merged together

D2B

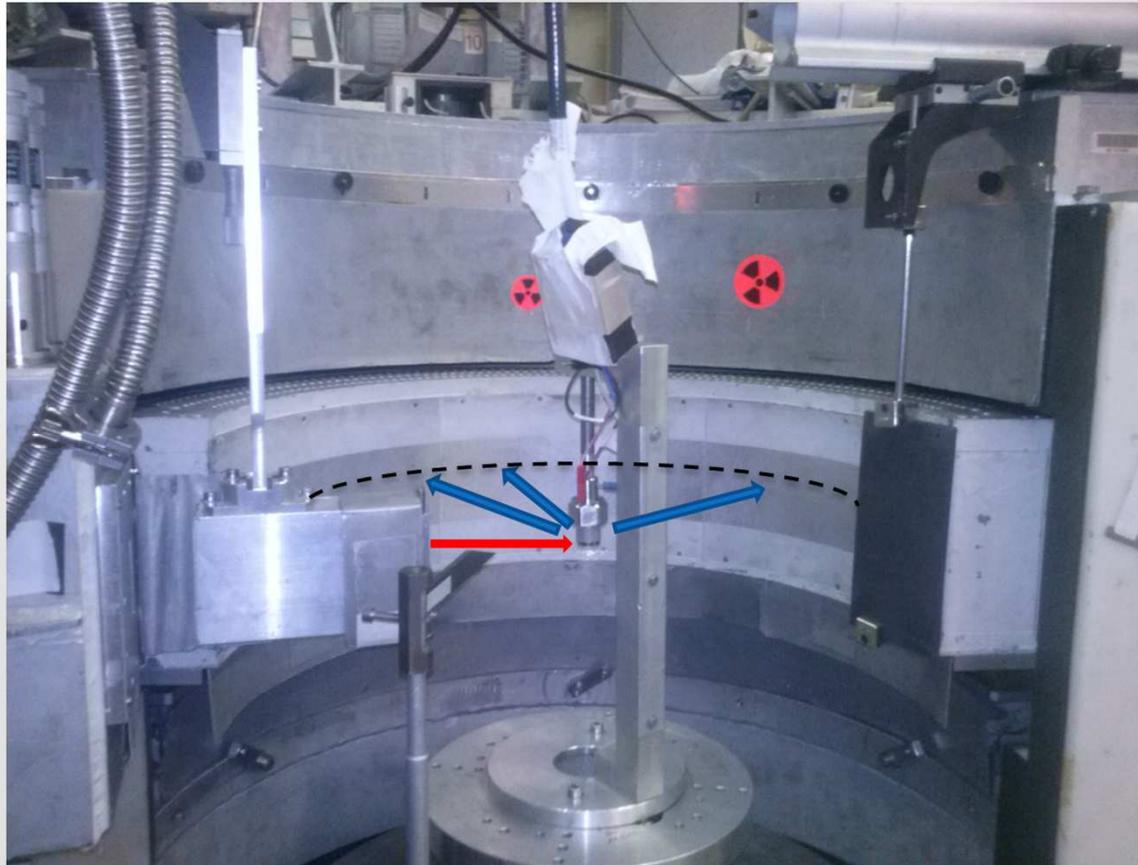


High resolution diffractometer  
1 pattern=2-5 hours

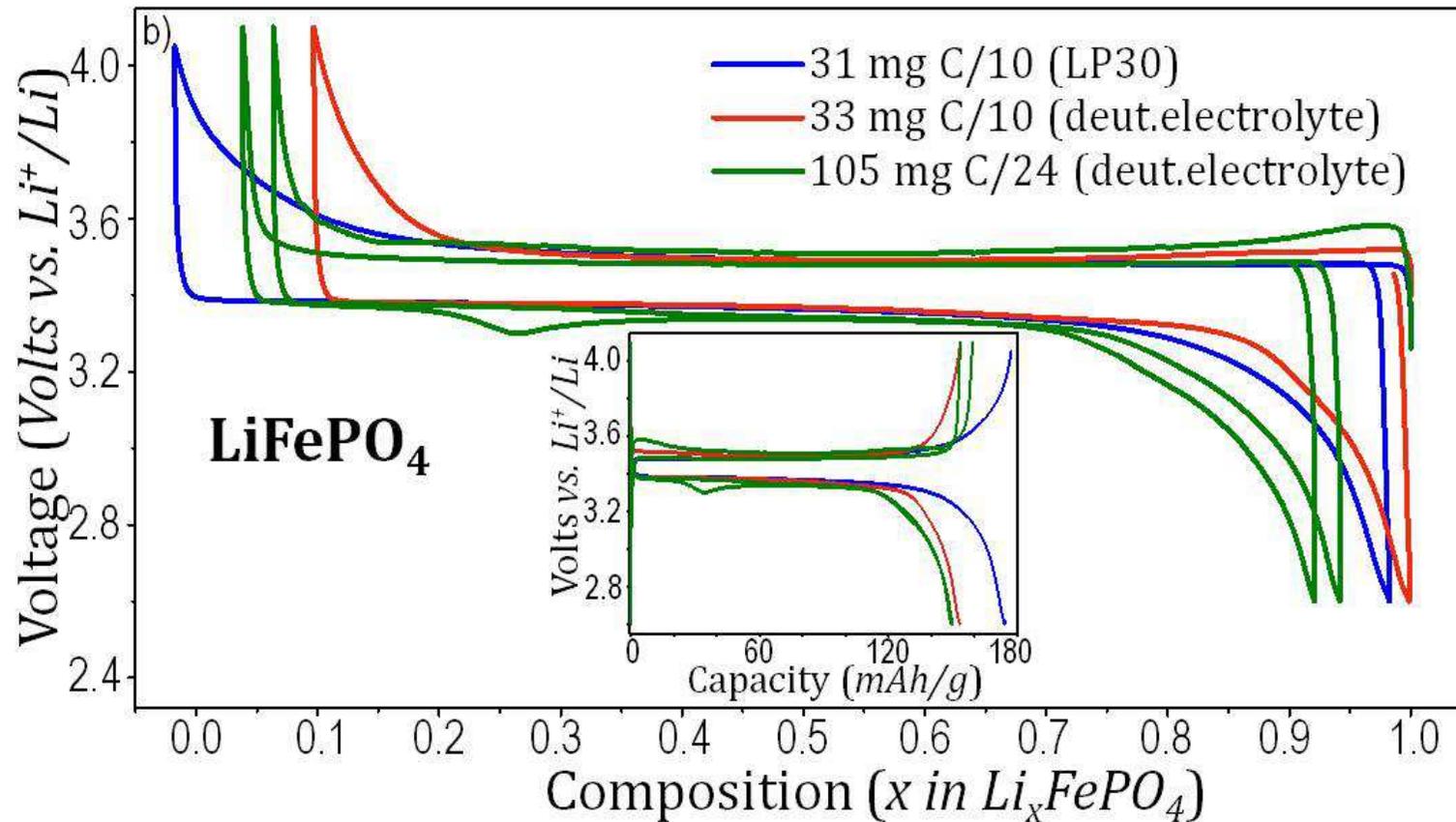
# A new electrochemical cell for in-situ NPD



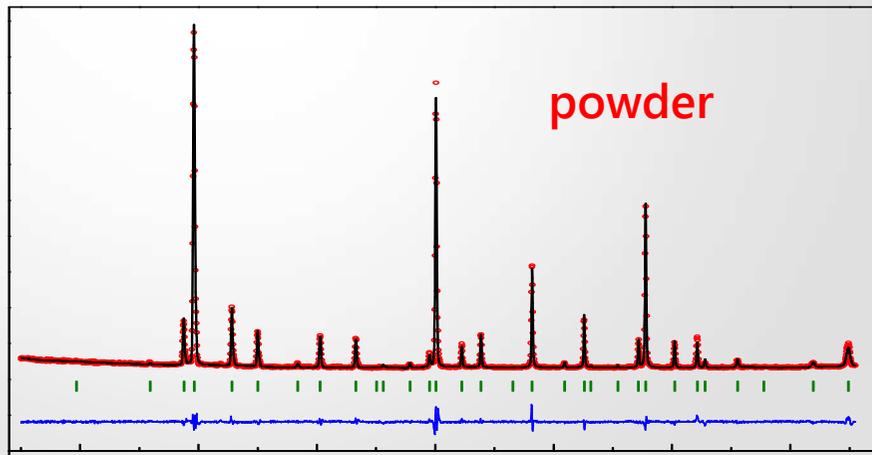
# D20 @ ILL : Experiment Setup



# Validation of the cell : $\text{LiFePO}_4$

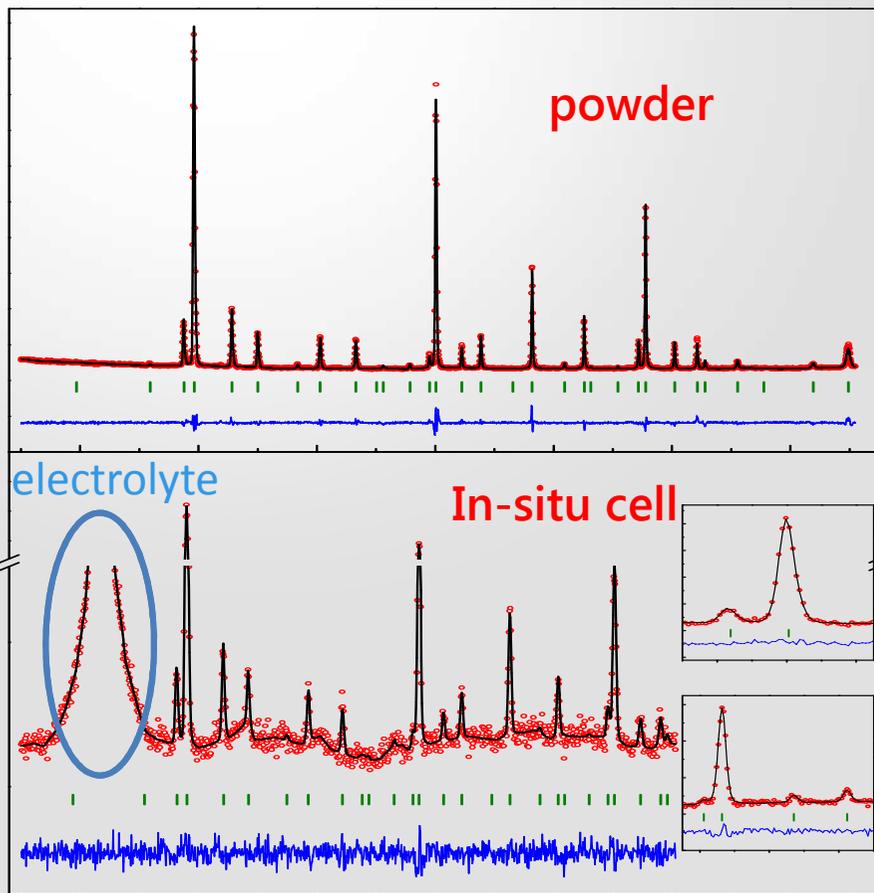


## Validation of the cell : $\text{LiFePO}_4$



$\text{LiFePO}_4$  POWDER  
measured from **High Resolution**  
Neutron Diffractometer  
**D2B** at ILL Grenoble

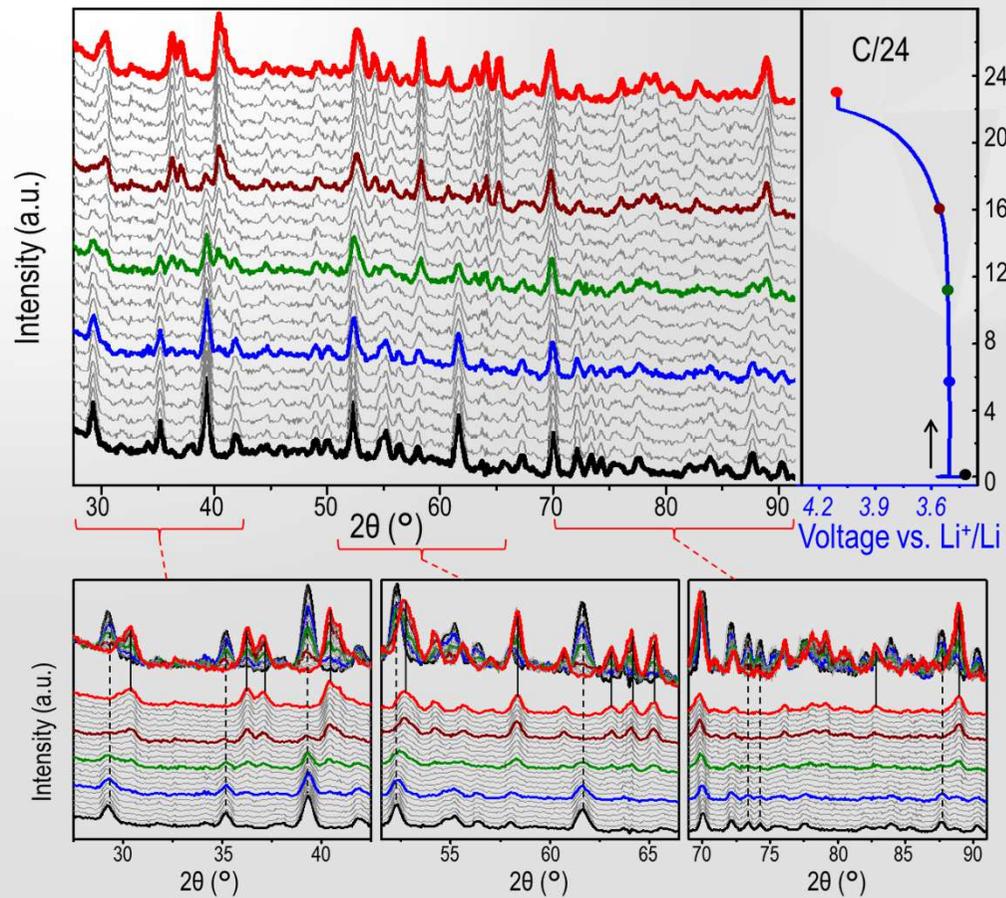
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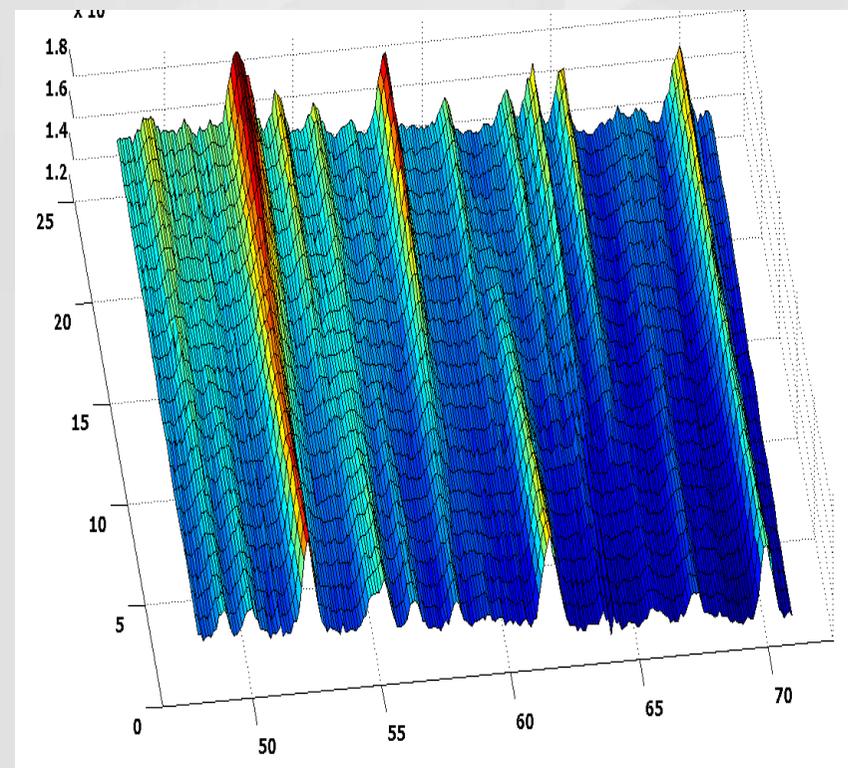
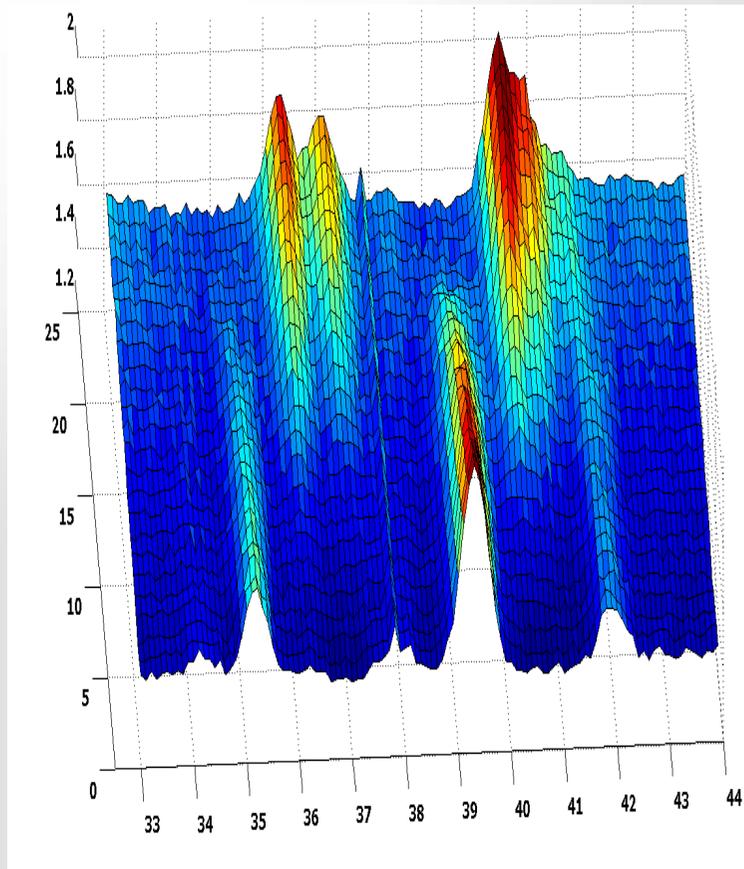
$\text{LiFePO}_4$  ELECTRODE  
in the in-situ cell,  
in a full-battery configuration,  
measured from **High Flux**  
Neutron Diffractometer  
**D20** at ILL Grenoble

# Validation of the cell : $\text{LiFePO}_4$

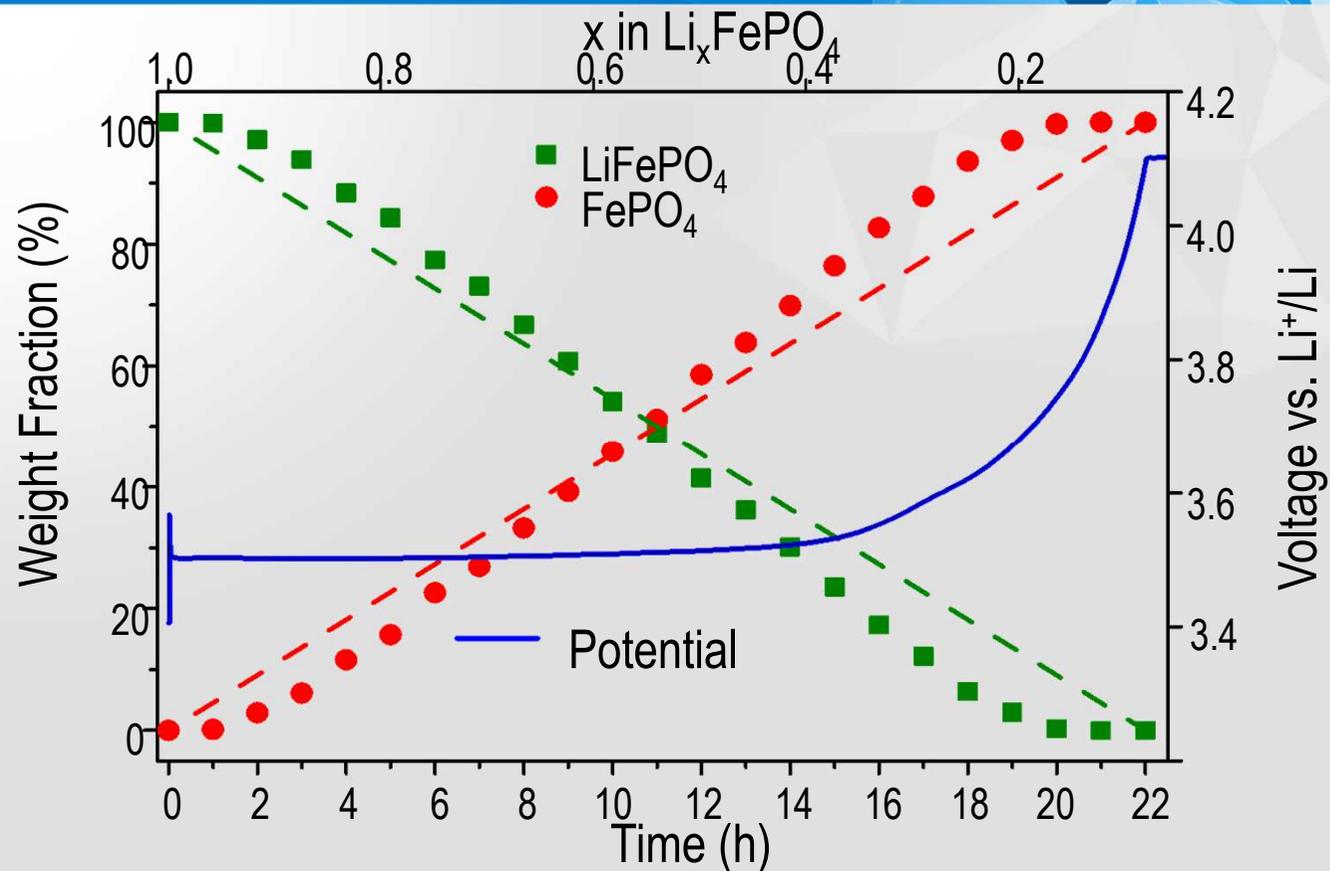


1 hour scan  $\equiv \Delta x = 0.042 \text{ Li}$

# Validation of the cell : $\text{LiFePO}_4$



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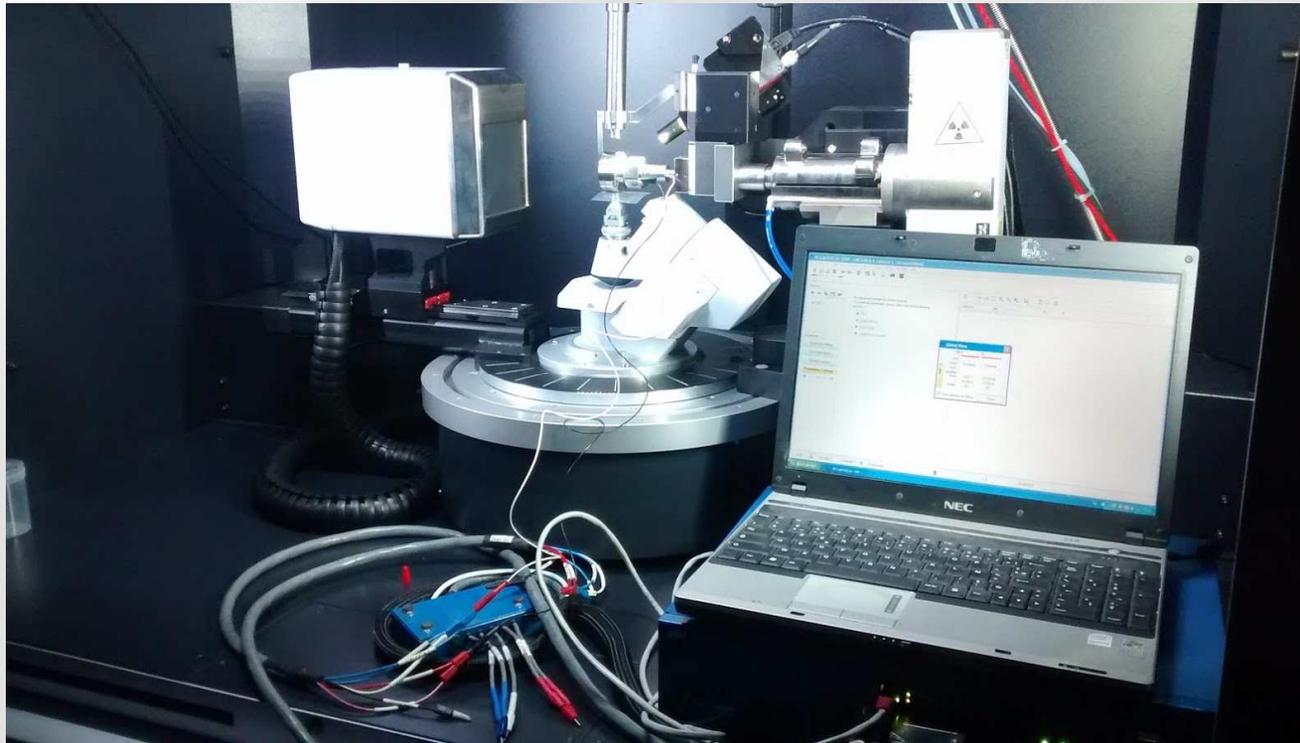
M. Bianchini et al, *J. Electrochem. Soc.*, 160(11), A2176, 2013

# Conclusion

- ▶ **Diffraction is an essential for the search of materials for Li and Na batteries**
  - NEW materials, new structures
  - Materials stoichiometries, defects, charge ordering
  - Mechanisms of Li<sup>+</sup> insertion/extraction (reversibility/metastable phases)
- ▶ **Neutron, Synchrotron but also Lab X-rays sources may be used once appropriate operando/in-situ cells are designed: the best is to use all of them ! !**
- ▶ **A Ti-Zr cell, fully transparent to neutrons + high flux neutron source provides high quality data for Rietveld refinement**
- ▶ **A fully Li<sup>+</sup> and Mn<sup>3+</sup>/Mn<sup>4+</sup> ordered composition was spotted for  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$**

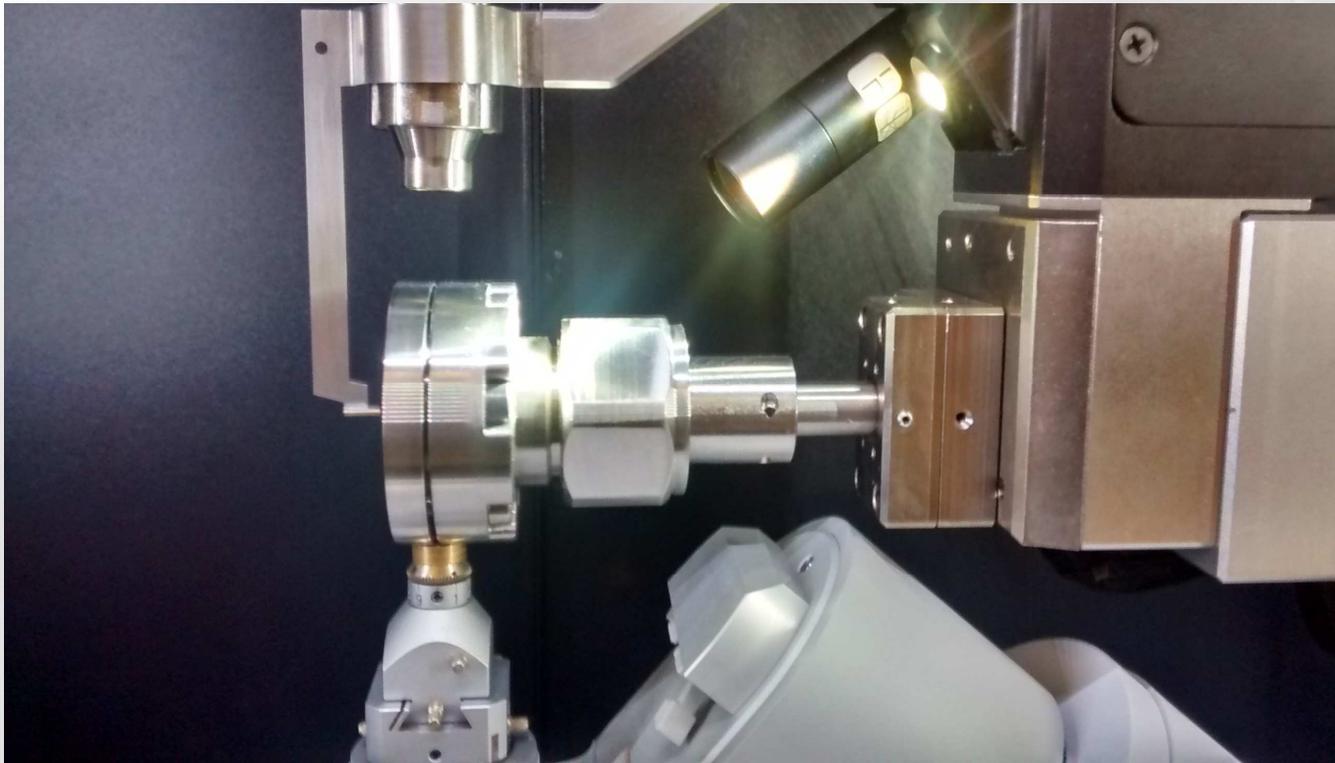
# What's Next ?

Powder diffraction & cycling  
in the single crystal diffractometer



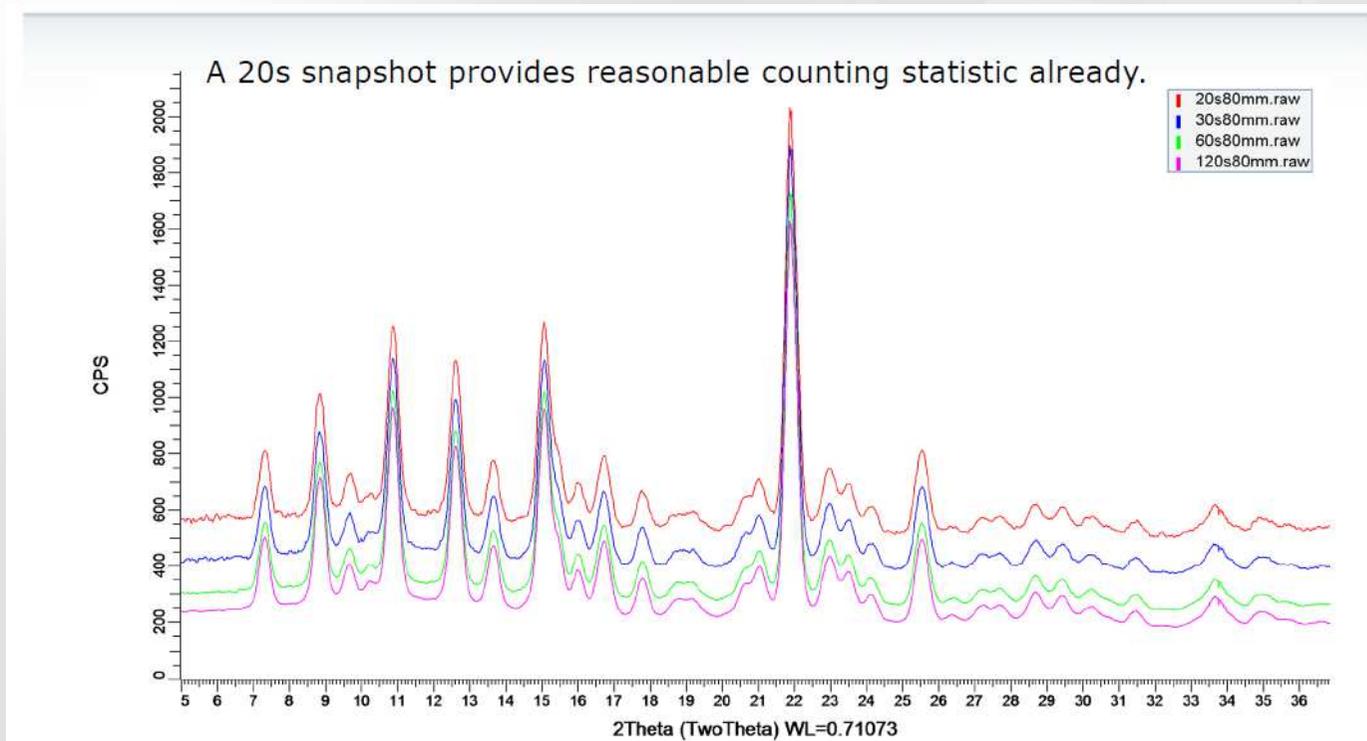
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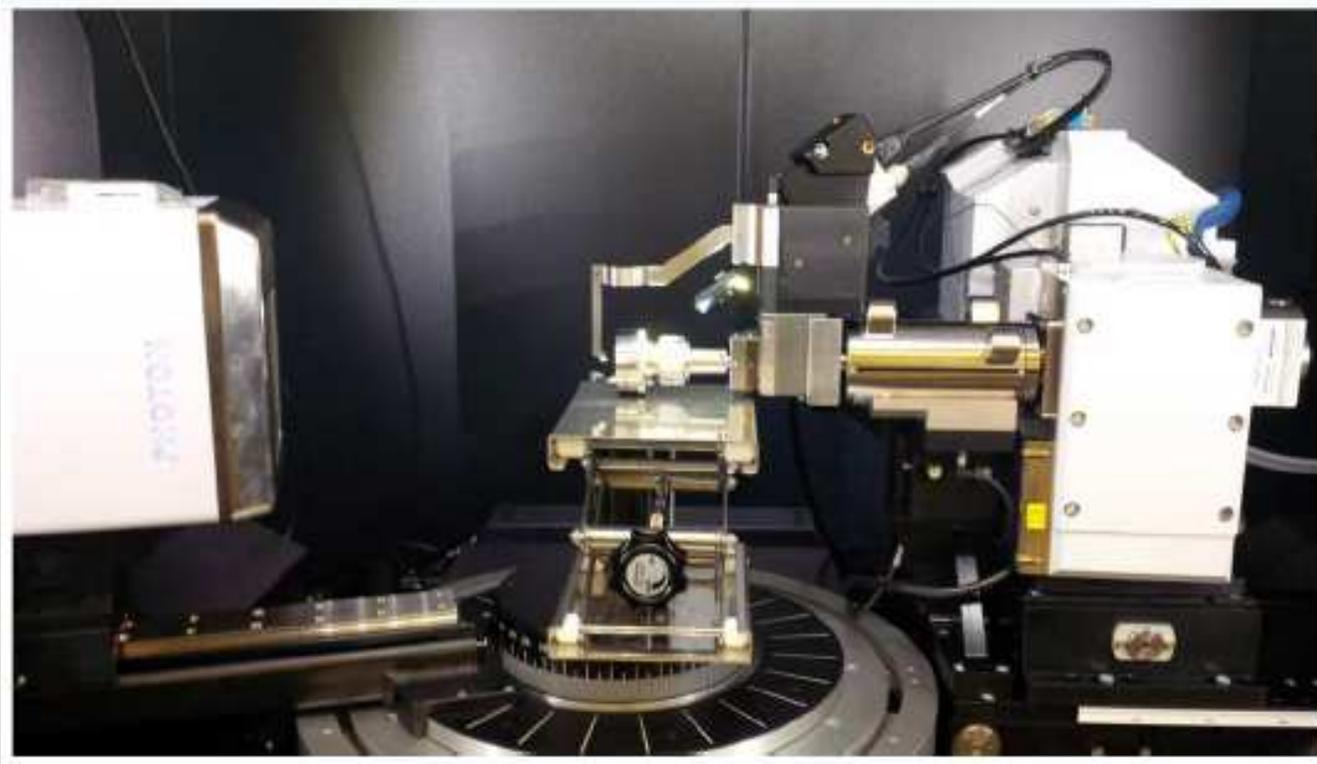
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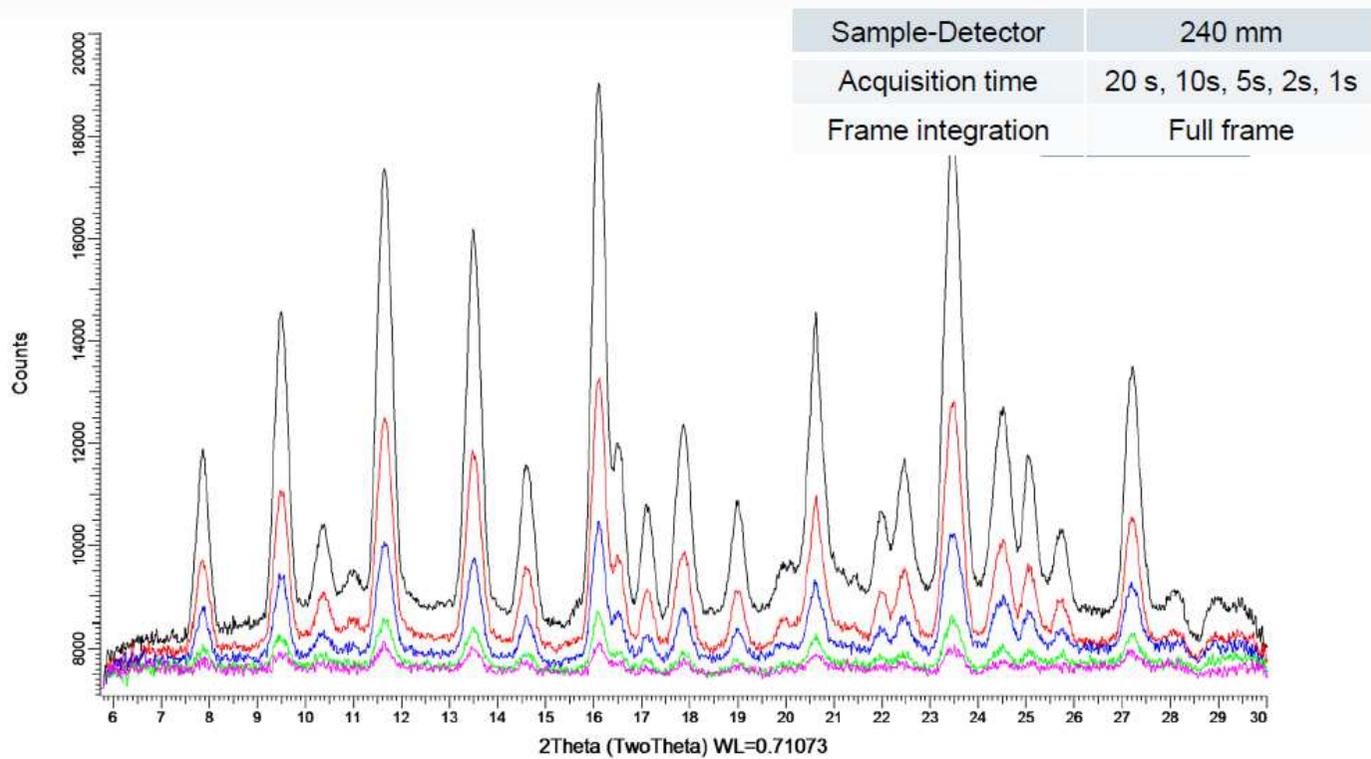


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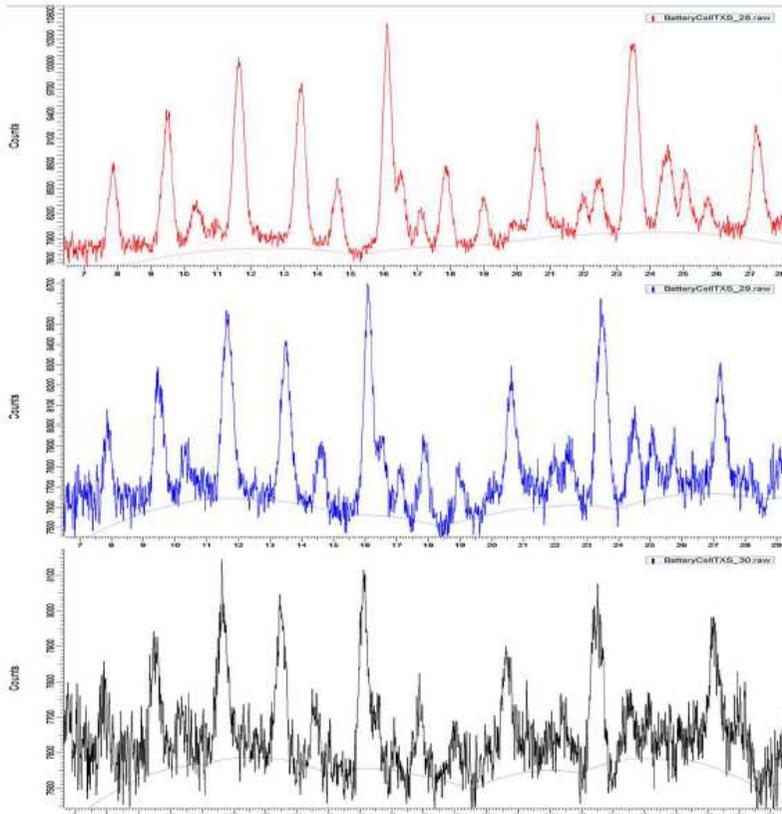
Mo TXS source



# What's Next ?



# What's Next ?



|                   |            |
|-------------------|------------|
| Sample-Detector   | 240 mm     |
| Acquisition time  | 5s         |
| Frame integration | Full frame |

|                   |            |
|-------------------|------------|
| Sample-Detector   | 240 mm     |
| Acquisition time  | 2s         |
| Frame integration | Full frame |

|                   |            |
|-------------------|------------|
| Sample-Detector   | 240 mm     |
| Acquisition time  | 1s         |
| Frame integration | Full frame |

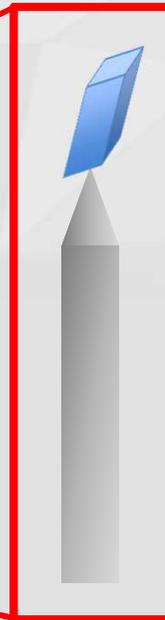
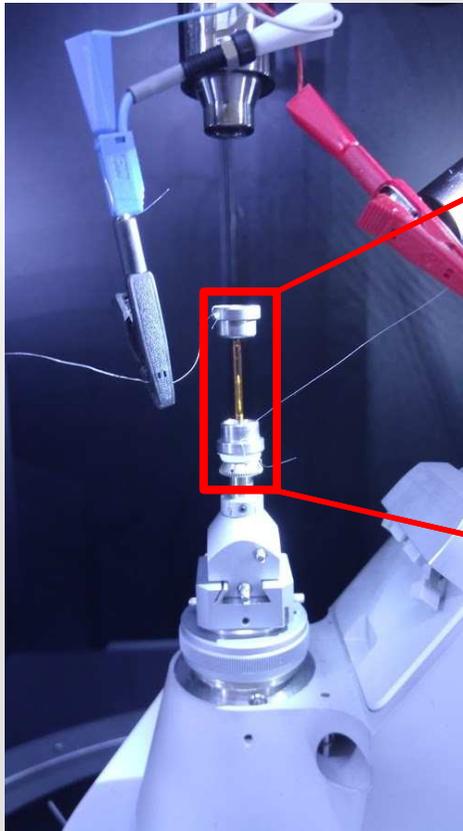
# What's Next ?

Can we cycle 1 single Crystal??

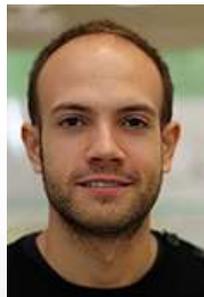


# What's Next ?

Can we cycle 1 single Crystal??



# Aknowledgements



**C. Masquelier (LRCS)**  
**M. Bianchini (Berkeley)**  
**L. Croguennec (ICMCB)**  
**F. Chen (LRCS)**

**E. Suard, J. Rodriguez-Carvajal (ILL)**  
**F. Fauth (ALBA Synchrotron)**  
**M. Morcrette, J. B. Leriche (LRCS)**

