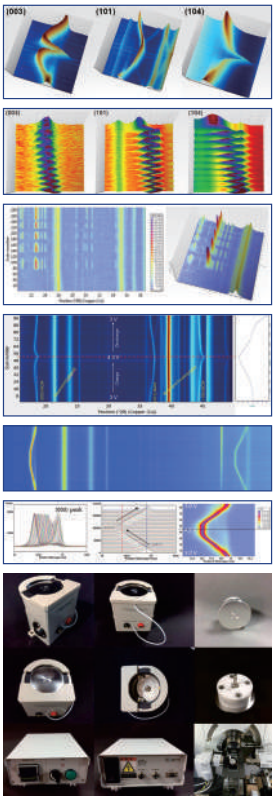
PDC TECH
PROCESS DEVELOPE CORP

JAI CELL :
In-situ Battery Test

Perform the work of the accelerator in XRD.

- JAI Cell developed to measure the electrode reactions which occur during charging and discharging with XRD or Neutron.
- JAI CELL, the latest model to the successful in-situation baatery test.
- X-ray and Neutron characterization in the reflective mode.
- Easy assembly / disassemblely and cleaning.



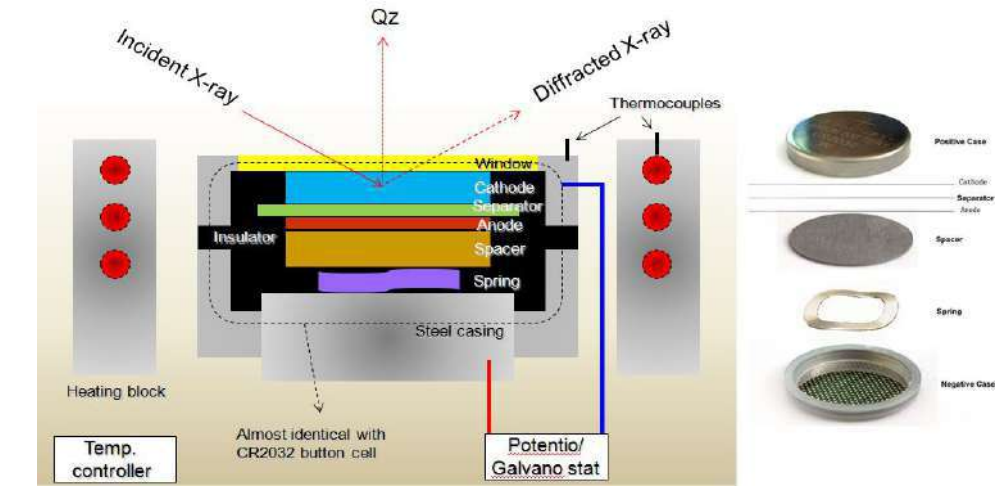
The In-situation system Company

In-situ XRD Analysis System of Lithium-ion Secondary Batteries

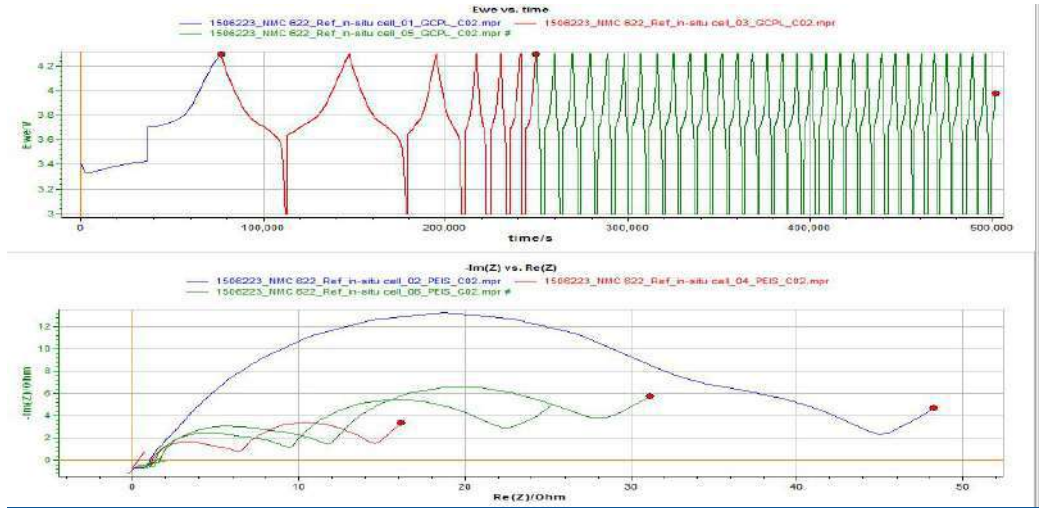
PDC TECH
PROCESS DEVELOPE CORP

It is important to study the mechanism of the positive electrode material when studying materials in secondary Li-ion batteries. In particular, the cathode reactions which is occured charging and discharging are particularly important. XRD is a good way to analyze the structure of the materials in secondary Li-ion batteries. However, It is hard to measure the same time while performing the charging and discharging.
"In-situ XRD Analysis System" makes it possible to measure these changes.

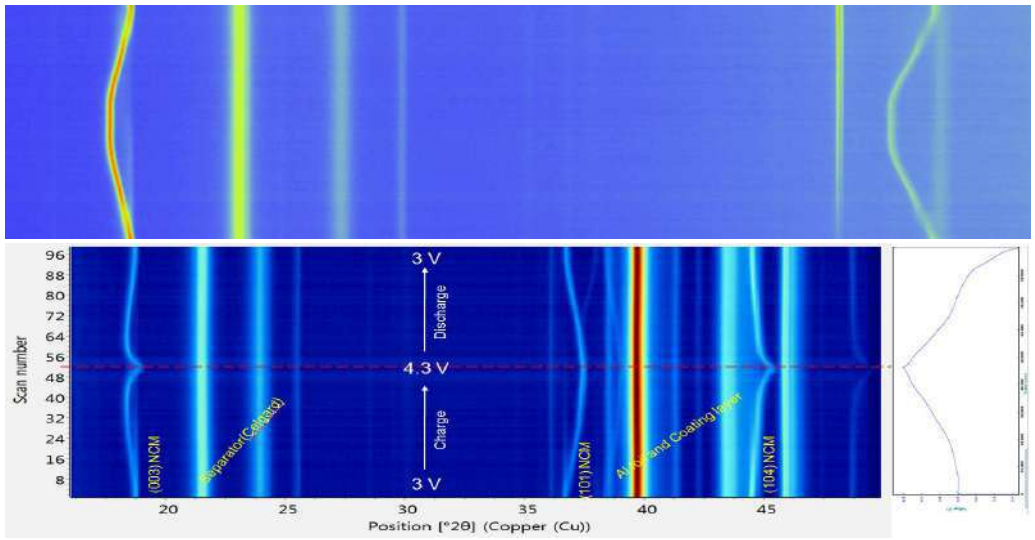
In-situ XRD Analysis System into heater



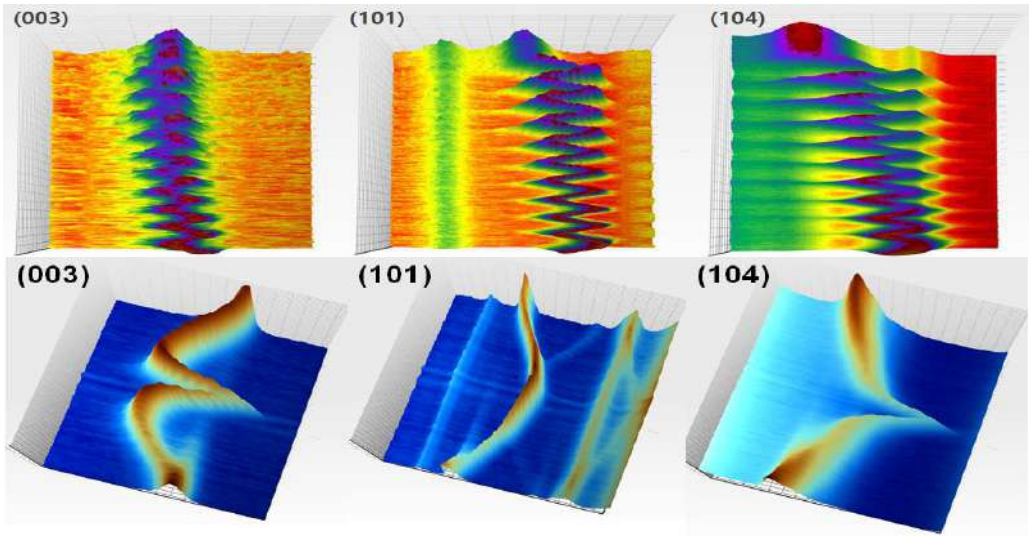
Charge/Discharge Data (NMC : 0.1C, 0.2C, 1C)



XRD Data with Charge/Discharge (2theta:15~60, LCO/NMC)



XRD Data with Charge/Discharge (ZOOM IN: OLO, NMC)



PDC TECHNOLOGY 17-1, Gwangneungnae-ro, Jinjeop-eup, Namyangju-si, Gyeonggi-do, KOREA (ZIP:153-846) Phone : +82-11-9539-3615 E-mail : pdctech@pdctech.co.kr

Instruction Configuration for ISBC

(ISBC : In-Situation Battery Cell)

In-Situation Battery Cell for XRD

Model : ISBC-PAN-H102

Revisions :

Revision	Date	Initials	Commnets
1	Nov 10, 2023	G.A KANG	First Draft
2			
3			
4			

References :

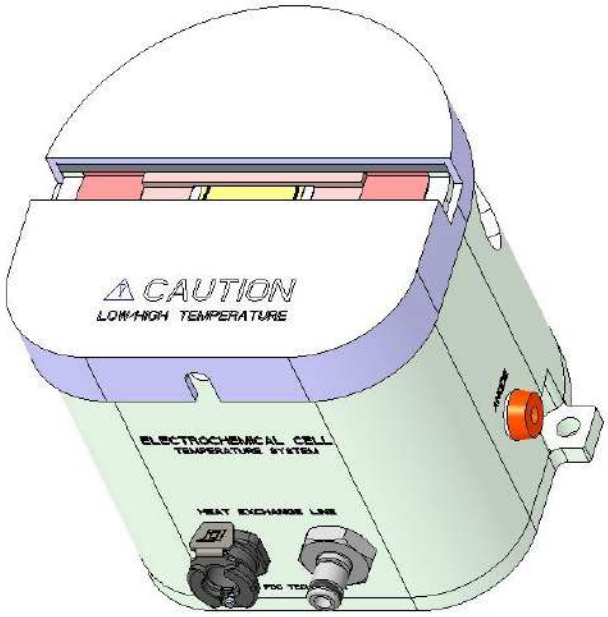
Ref No.	Documents ID	Initials

PDC TECHNOLOGY
17-1, Gwangneungnae-ro, Jinjeop-eup, Namyangju-si, Gyeonggi-do, KOREA (ZIP:12020)
Phone : +82-11-9539-3615

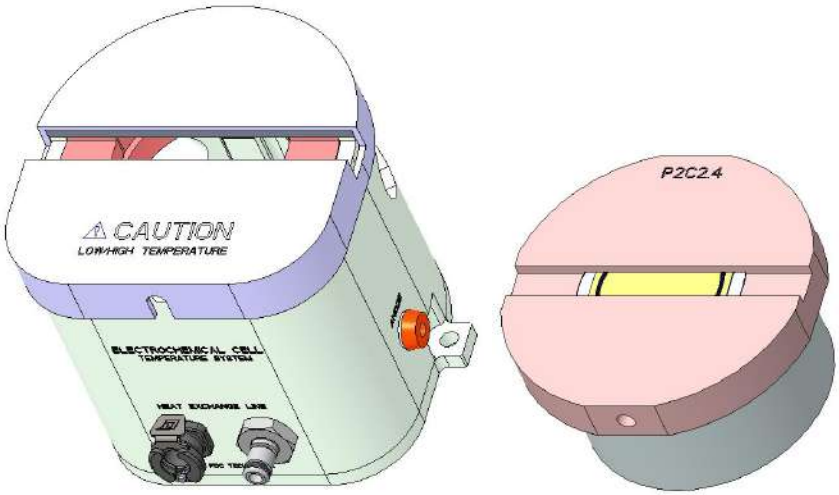
Contents :

1. 3D-CAD Configuration

This is the 3D design, In-situation Battery Cell system(ISBC).



External 3D view of ISBC module : ISBC-PAN-H100



External 3D view of heating & Cell module

2. Product Photos

This is the real product photos., In-situation Battery Cell system(ISBC).

PHOTO1. ISBC System on XRD

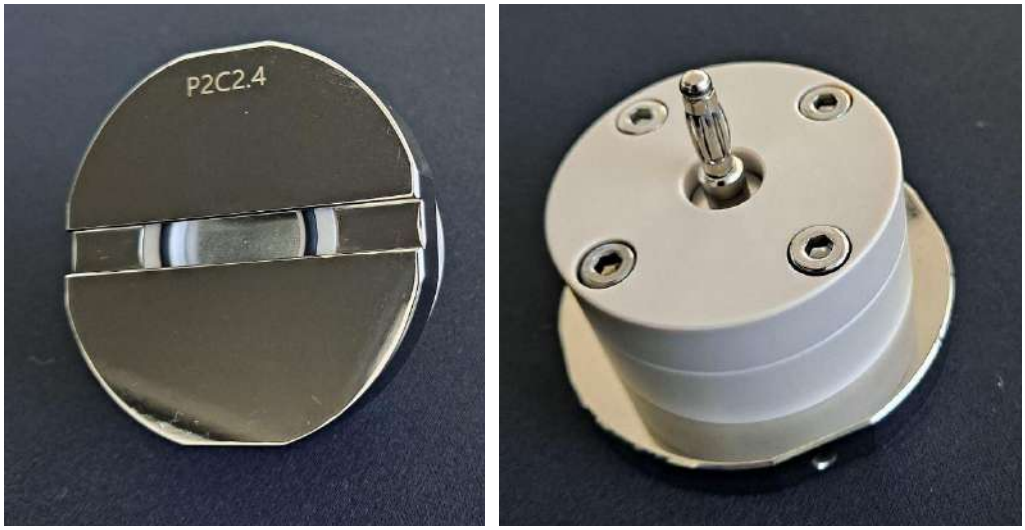


PHOTO2. Cell Module

PHOTO3. Heating Stage Module

ISBC for XRD
(ISBC : In-Situation Battery Cell)

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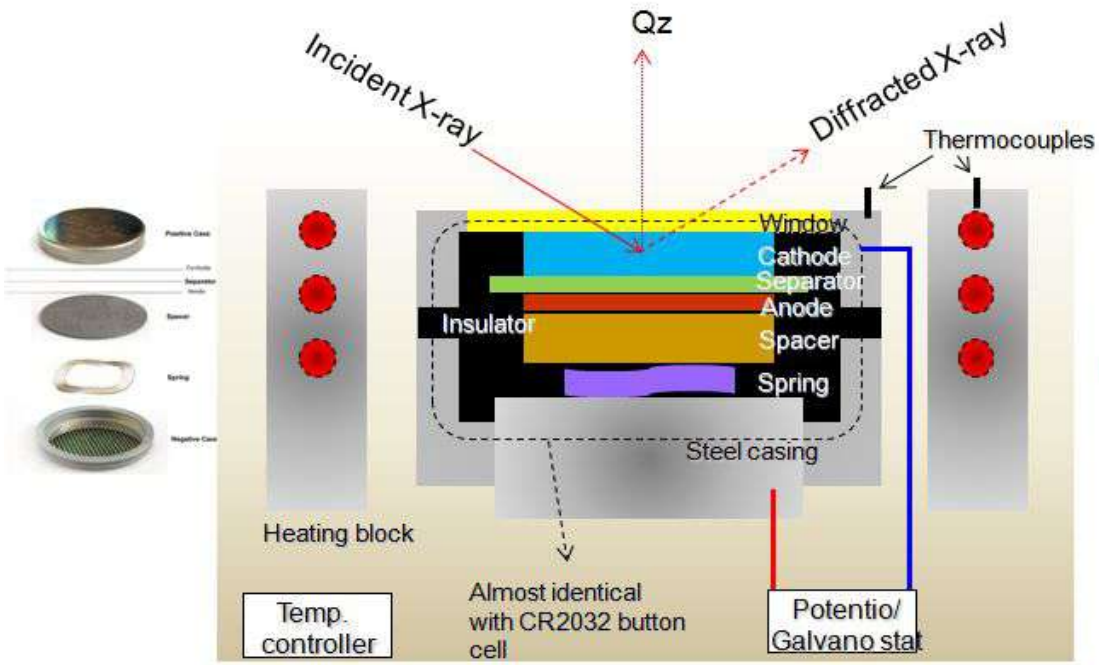
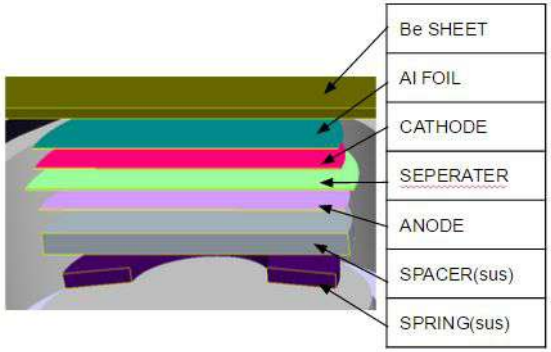
Phone : +82-70-4324-0810
Mobile Phone : +82-11-9539-3615

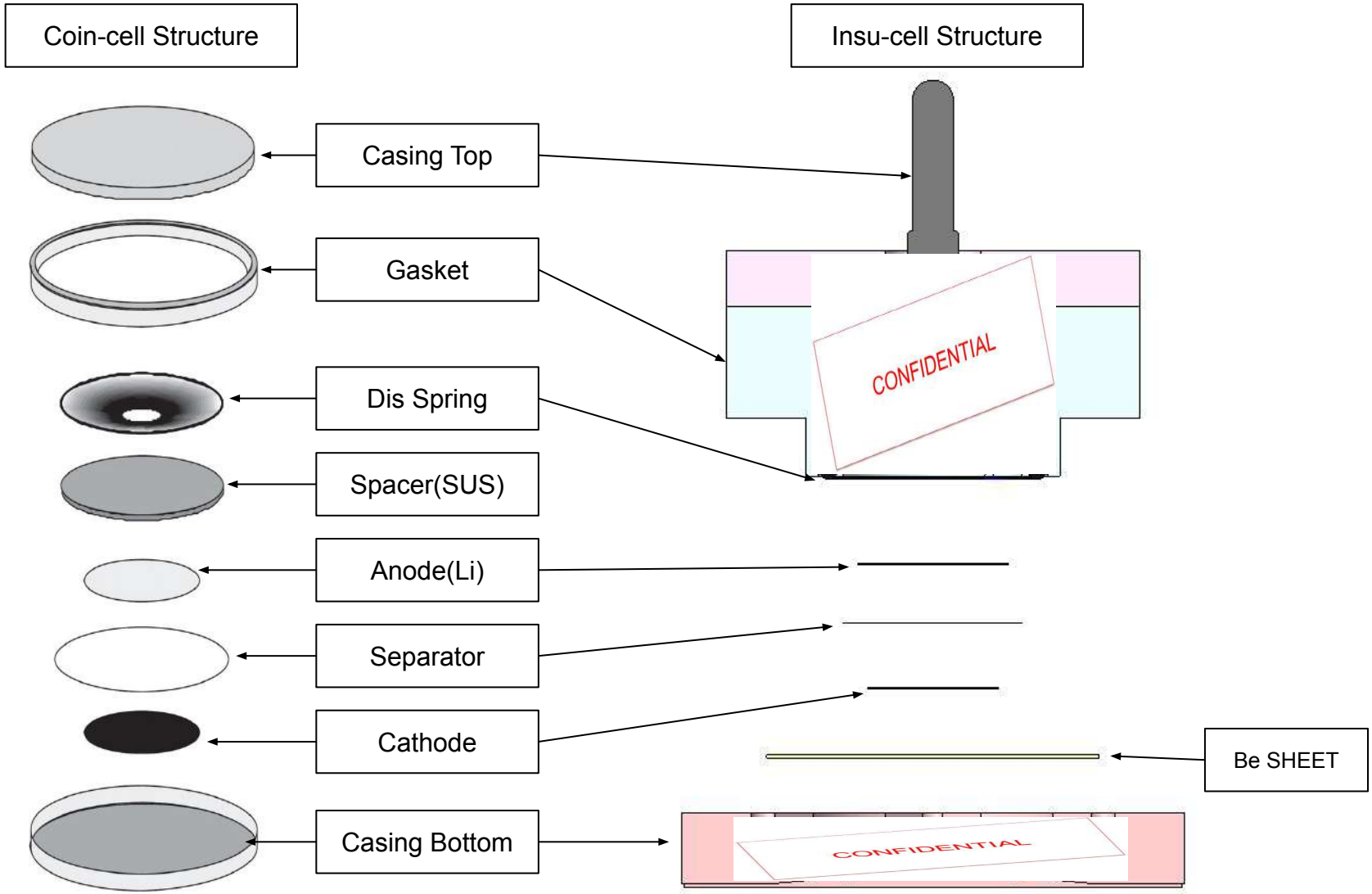


"Cycling + Heating"

It is important to study the mechanism of the positive electrode material when studying materials in secondary Li-ion batteries. In particular, the cathode reactions which is occured charging and discharging are particularly important. XRD is a good way to analyze the structure of the materials in secondary Li-ion batteries. However, It is hard to measure the same time while performing the charging and discharging.



COIN-CELL vs. INSU-CELL STRUCTURE



GENERAL SPECIFICATION

Measurement Range	Incident Angle(θ) from 2.4° Min. Measurement Angle(2θ) : 4.8°
Material of Current Collector	Anode side : Be sheet Cathode side : SUS316L
Material of Insulator	Teflon
Number of Poles	2 Poles
Temperature Range	-10 ~ 70℃
Sample Size	D > ø14mm (Recommend)
Sample Weight	W > 50mg (Recommend)
Seperator Size	D > ø18mm (Recommend)
Li Metal Size	D > ø16mm (Recommend)

CHARGE/DISCHARGE SPECIFICATION

Control Voltage range	±10V(standard) or customer , specified range
Compliance Voltage	±12V(standard) or customer , specified voltage
Control Current range	Control Current range 8 ranges (1A,100mA,10mA, 1mA,100uA,10uA,1uA,100nA) or customer specified range
LED	Run: 1ea, POT/GAL: 2ea, Irange: 8ea
Input impedance	10^10 Ohm
Cell Connection	4 probe type, alligator clip cables
Voltage Accuracy	<0.01% f.s
Current Accuracy	<0.01% f.s
Full Scale Ranges	±10V(Standard)
Resolution (16 Bits)	0.3mV(Standard)
Current Control & Measurement	
Full Scale Ranges	±1A, ±100mA, ±10mA, ±1mA, , ±100uA, ±10uA, ±1uA, ±100nA(Standard)
Resolution 16 bit(0.0015% f.s)	Resolution 16 bit(0.0015% f.s)
Power	30Watt
Sampling time	> 50ms
PC communication	USB2.0

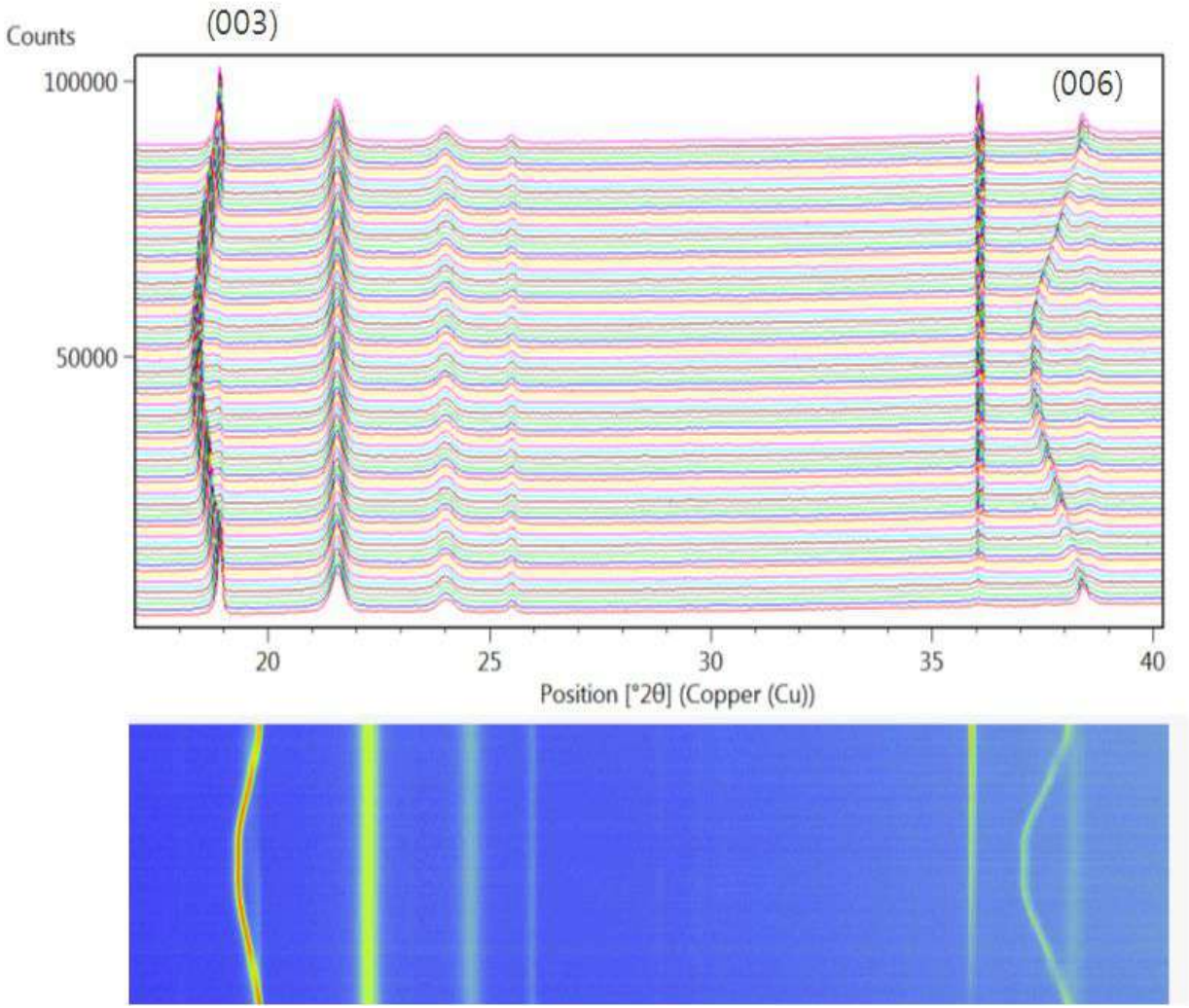
LiCoO2 powder had been provided by customer for the reliability of in-situ XRD system.

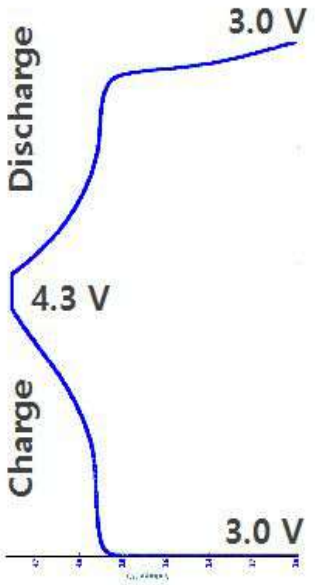
Sample preparation and electrochemical test conditions are following:

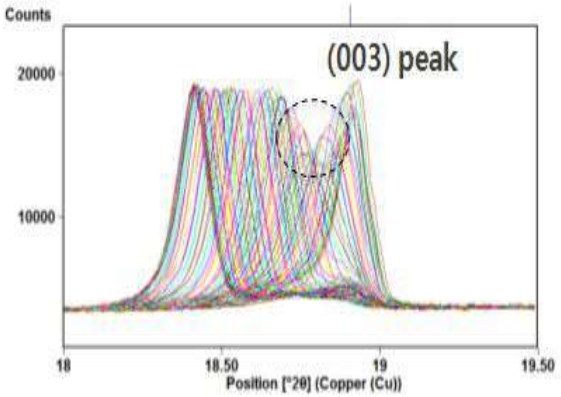
- Working electrode: LCO/NMC 80%, carbon 10% and PVdF 10% on a Aluminum foil
- Counter electrode: Lithium metal
- Electrolyte solution: $LiPF_6$ / EC:DMC=1:1
- Charge-discharge test:
- Current density: 0.1 C-rate
    - Voltage range: 3 ~ 4.3 V
    - # of cycle: 1 time
    - Room temperature

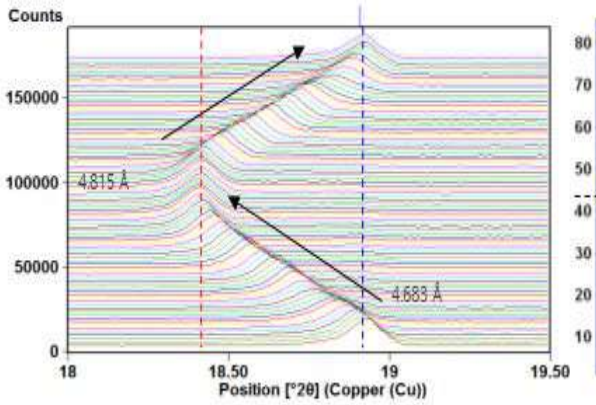
XRD test

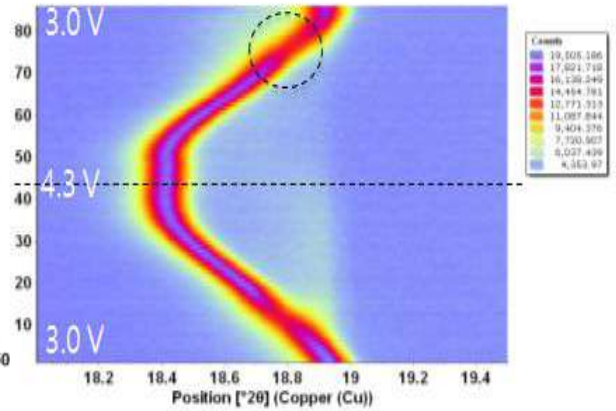
- Cu anode / BBHD / ISBC / PIXcel
- 10 min per scan

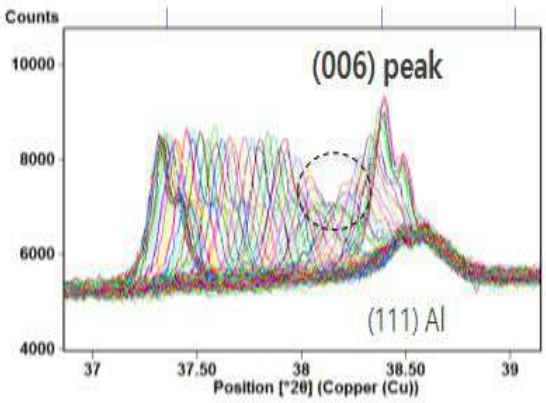

Counts
(003)
(006)
100000
50000
20
25
30
35
40
Position [°2θ] (Copper (Cu))

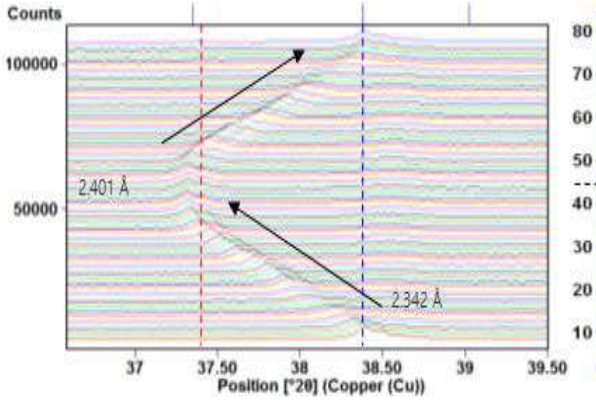

3.0 V
Discharge
4.3 V
Charge
3.0 V

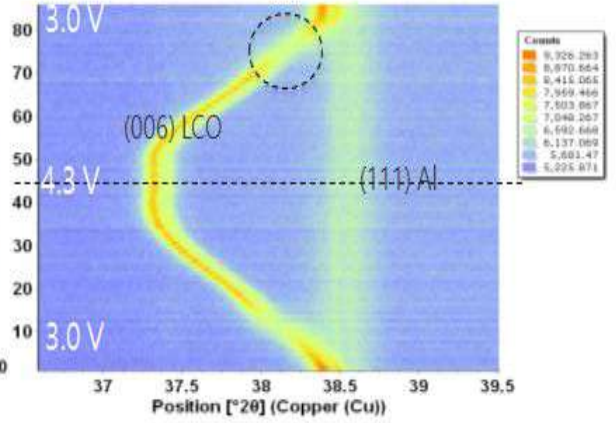




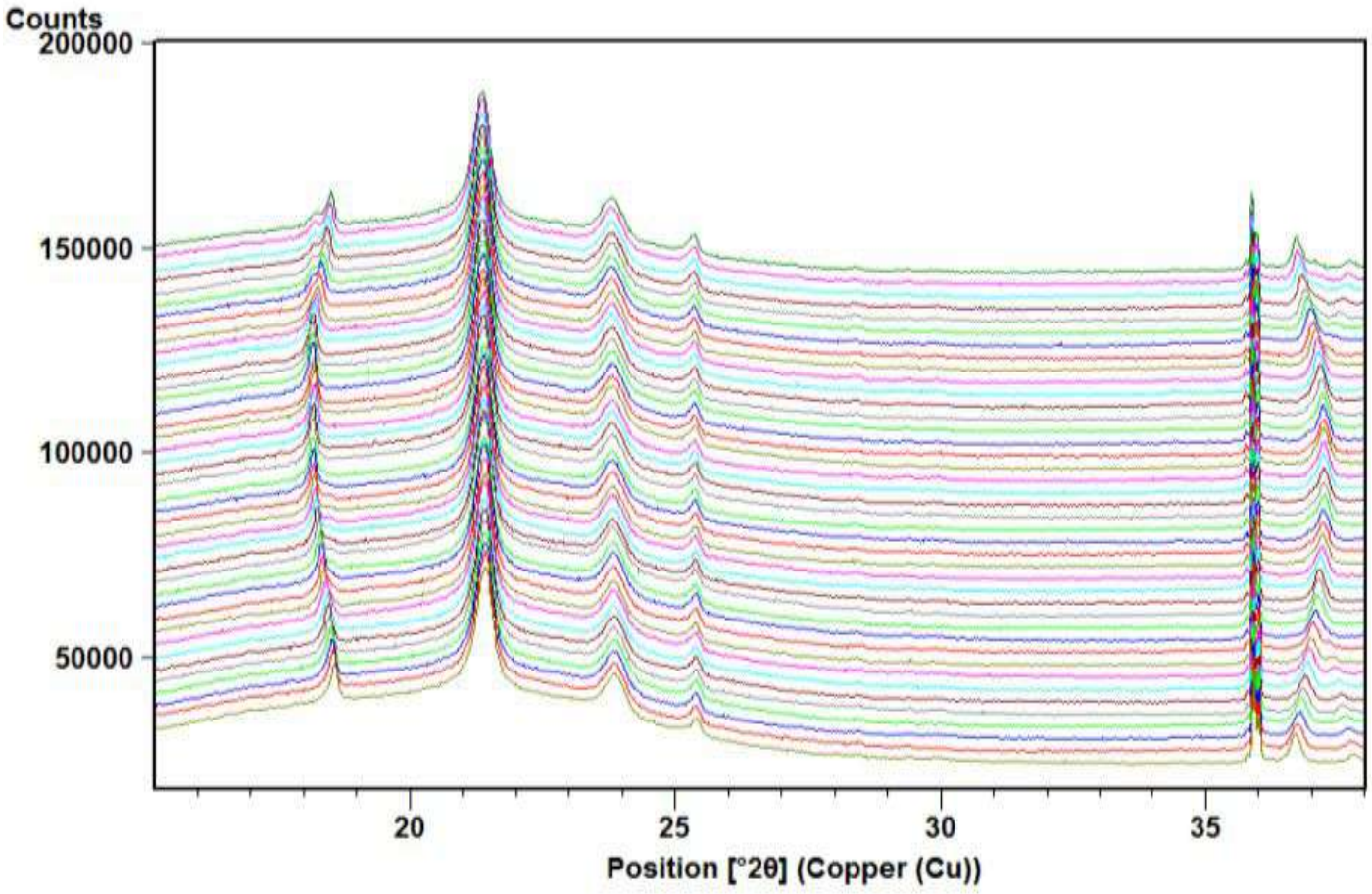


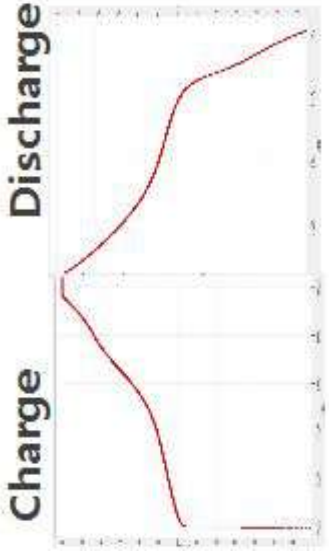




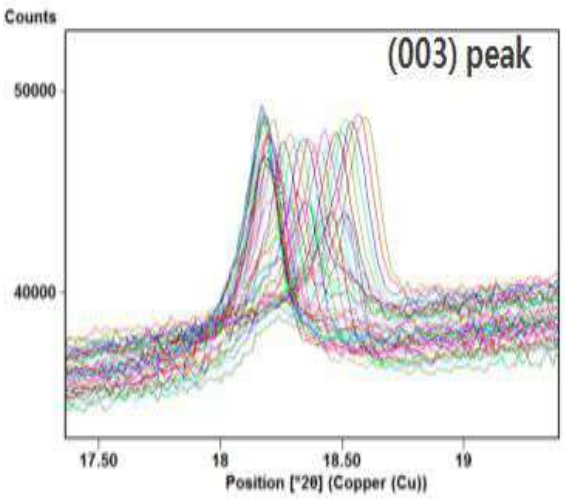


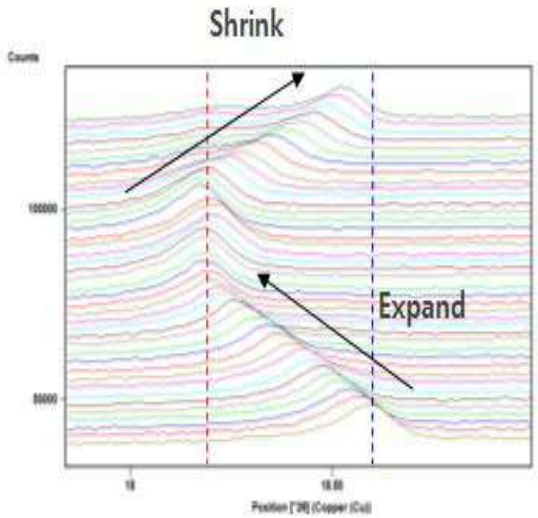
(003) and (006) peaks show a reversible behavior as a function of applied current, while (111) Al of substrate peak is keeping its position.

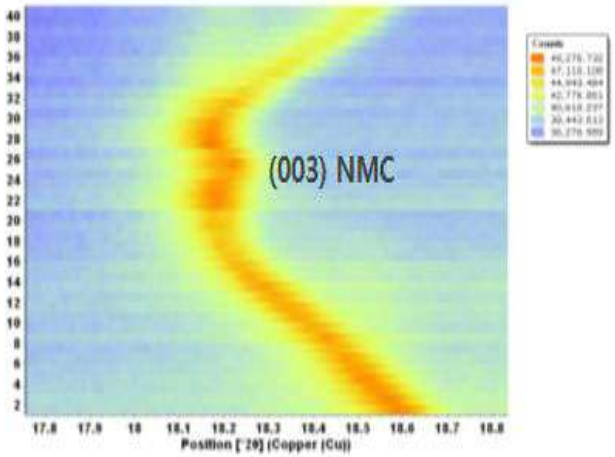


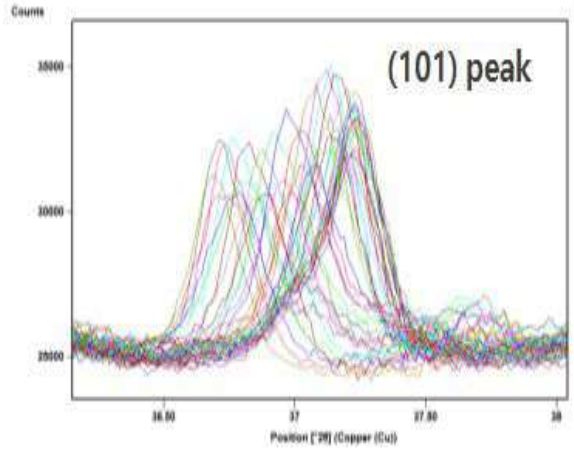


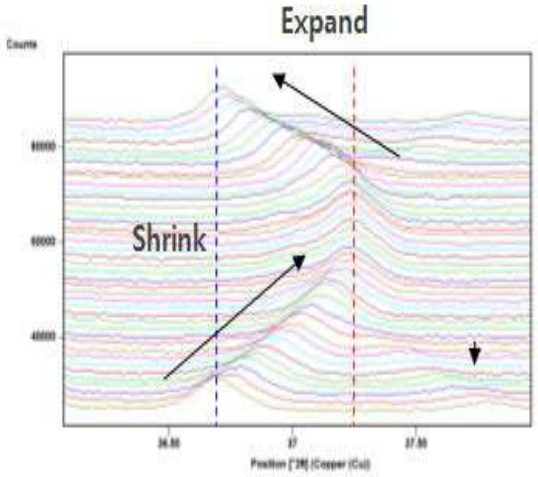
(003) And (101) peaks are shifted to opposite directions due to its intrinsic c/a ratio.

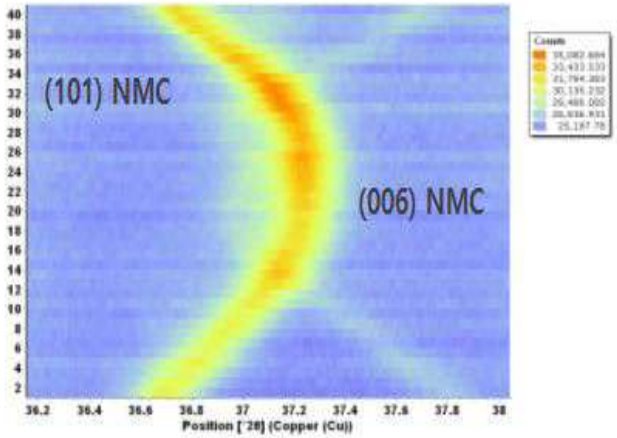

Counts
(003) peak
50000
40000
17.50
18
18.50
19
Position [°2θ] (Copper (Cu))


Shrink
Expand


(003) NMC
Position [°2θ] (Copper (Cu))


(101) peak
Position [°2θ] (Copper (Cu))


Expand
Shrink


(101) NMC
(006) NMC
Position [°2θ] (Copper (Cu))

NCM powder had been provided by customer for the reliability of in-situ XRD system.

Sample preparation and electro-chemical test conditions are following:

- Working electrode: NCM 80%, carbon 10% and PVdF 10% on a Aluminum foil
- Counter electrode: Lithium metal
- Electrolyte solution: $LiPF_6$ / EC:DMC=1:1
- Charge-discharge test:
- Curr-ent density: 0.1 C-rate
  - Voltage range: 3 ~ 4.3 V
  - # of cycle: 1 time
  - Room temperature

XRD test

- Cu anode / BBHD / ISBC / PIXcel
- 10 min per scan

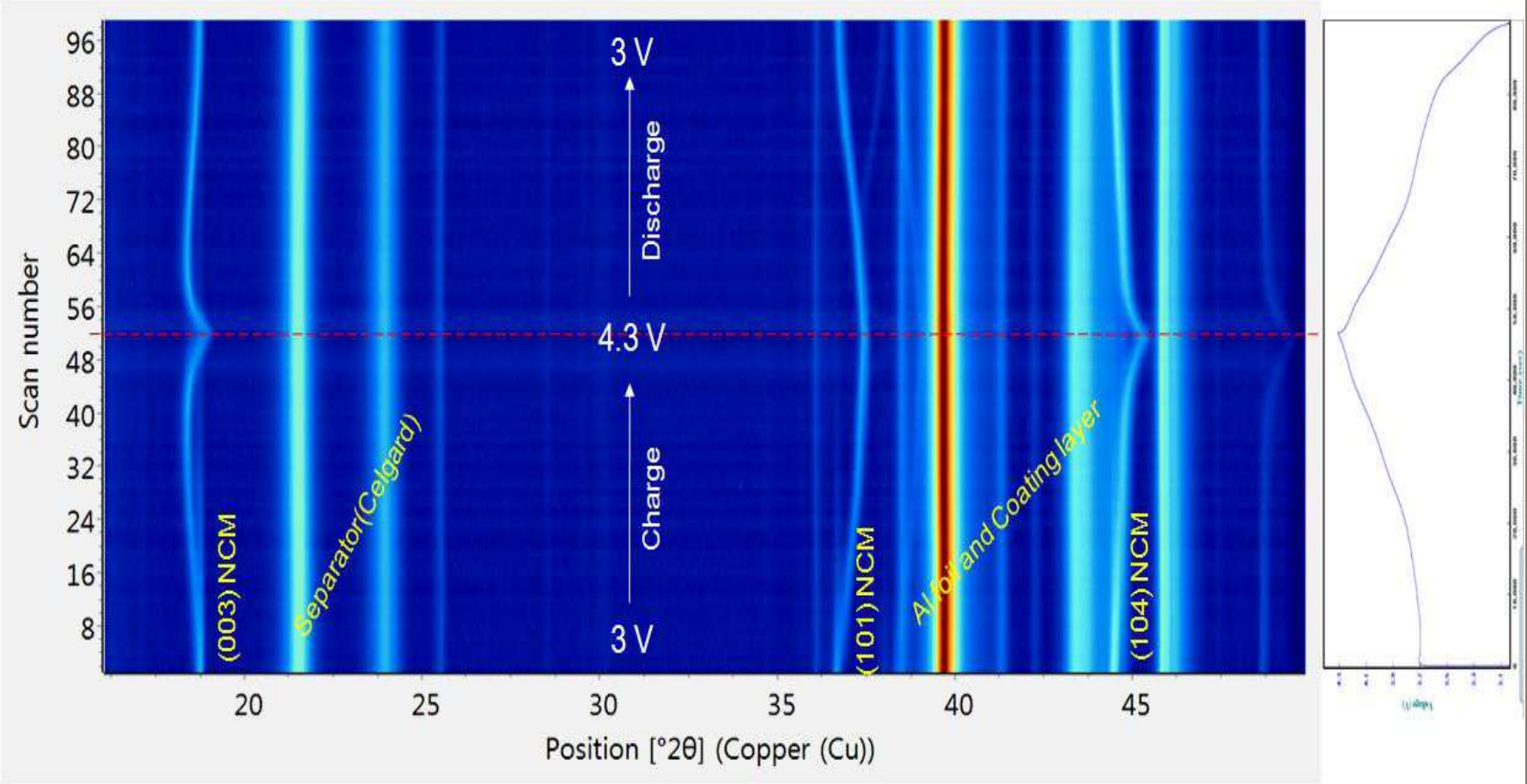


Figure. Overall XRD patterns of NCM @ 0.1 C-rate and 3.0 V to 4.3 V in CC/CC mode

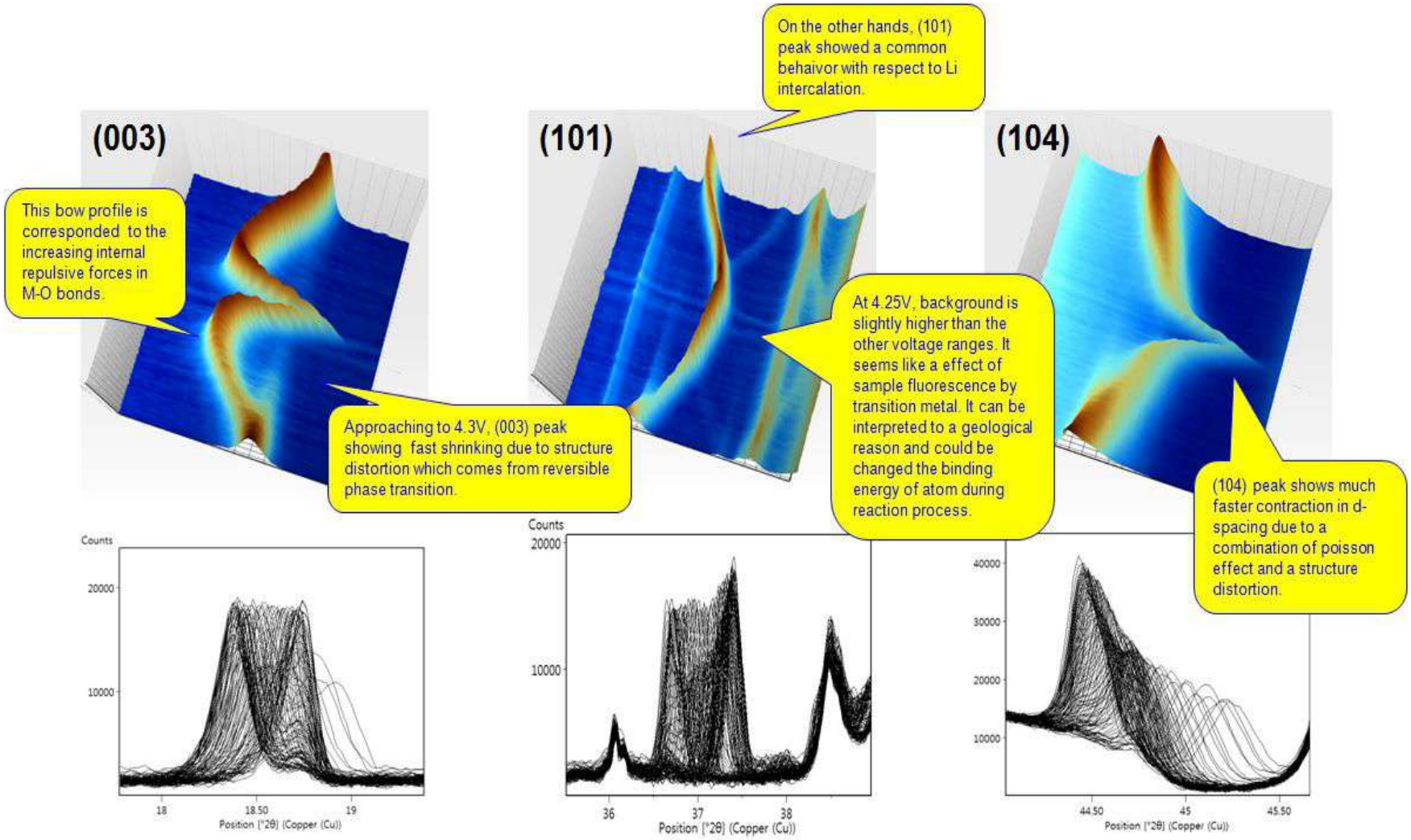
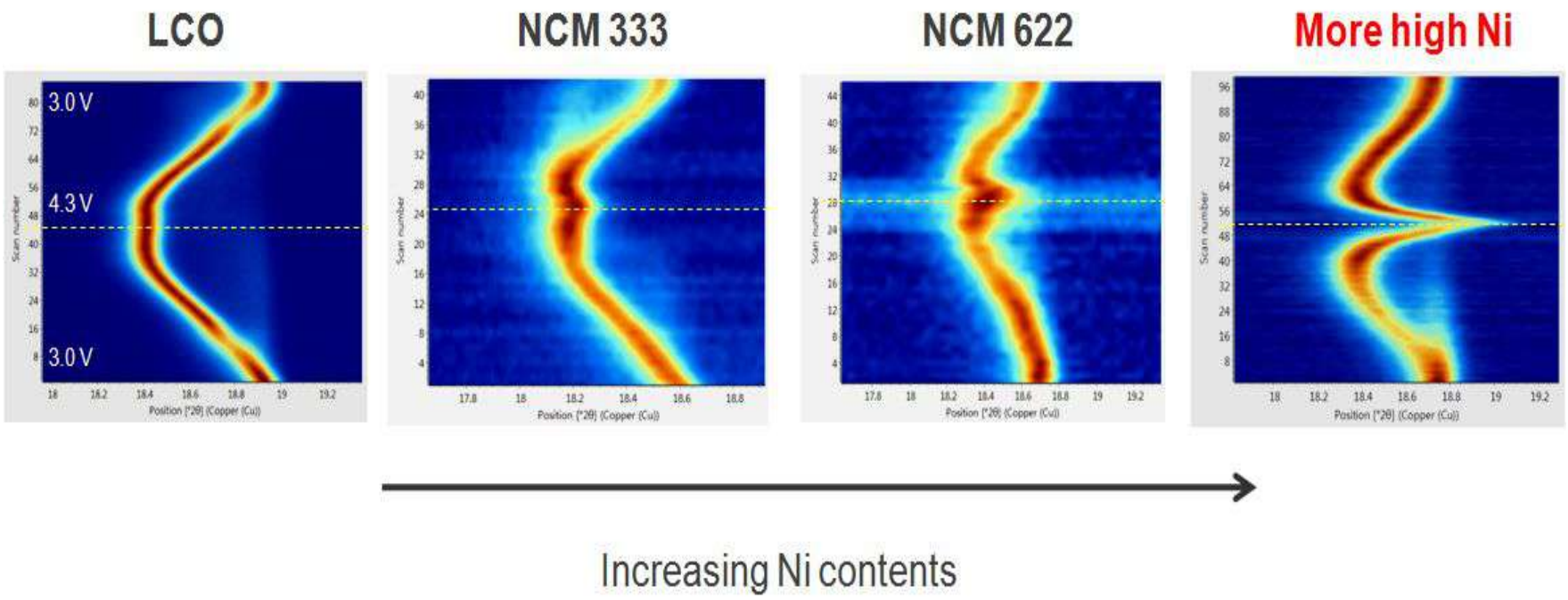
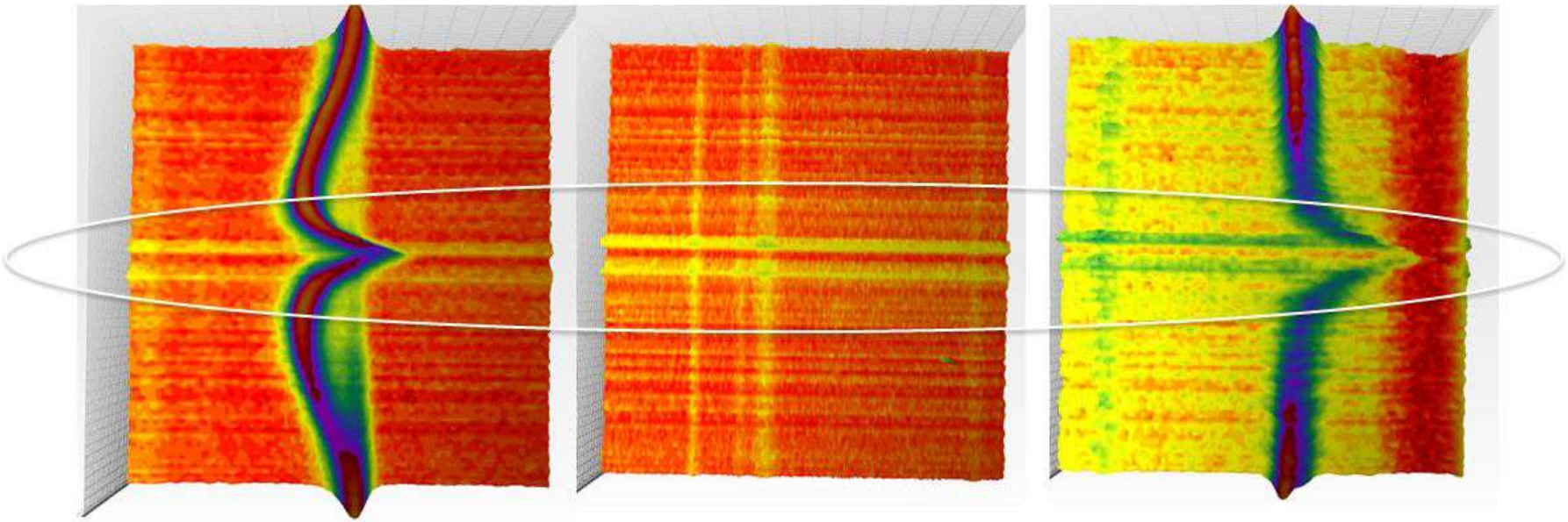


Figure. Detailed view of in-situ XRPD patterns of NCM with a various bragg diffraction plane.



With increasing Ni contents in a layered structure, a structure distortion at a higher voltage is increasing by a high lithium deficiency.



- Approaching to 4.3V, a background intensity has increased constantly regardless 2 theta range. It is assuming that some of transition metal ions have changing its binding energy resulting in a higher fluorescent signal to detector.

- It is called a geological effect of the sample against X-ray radiation. We used Cuka 8.04 keV, and it can easily excite transition metals in the structure. As a result, a detection sensitivity has been changed. This is usually detected in in-situ battery experiment, but nobody mentioned for this.

XRD DATA - EXPERIMENTAL : NMC (0.1C)

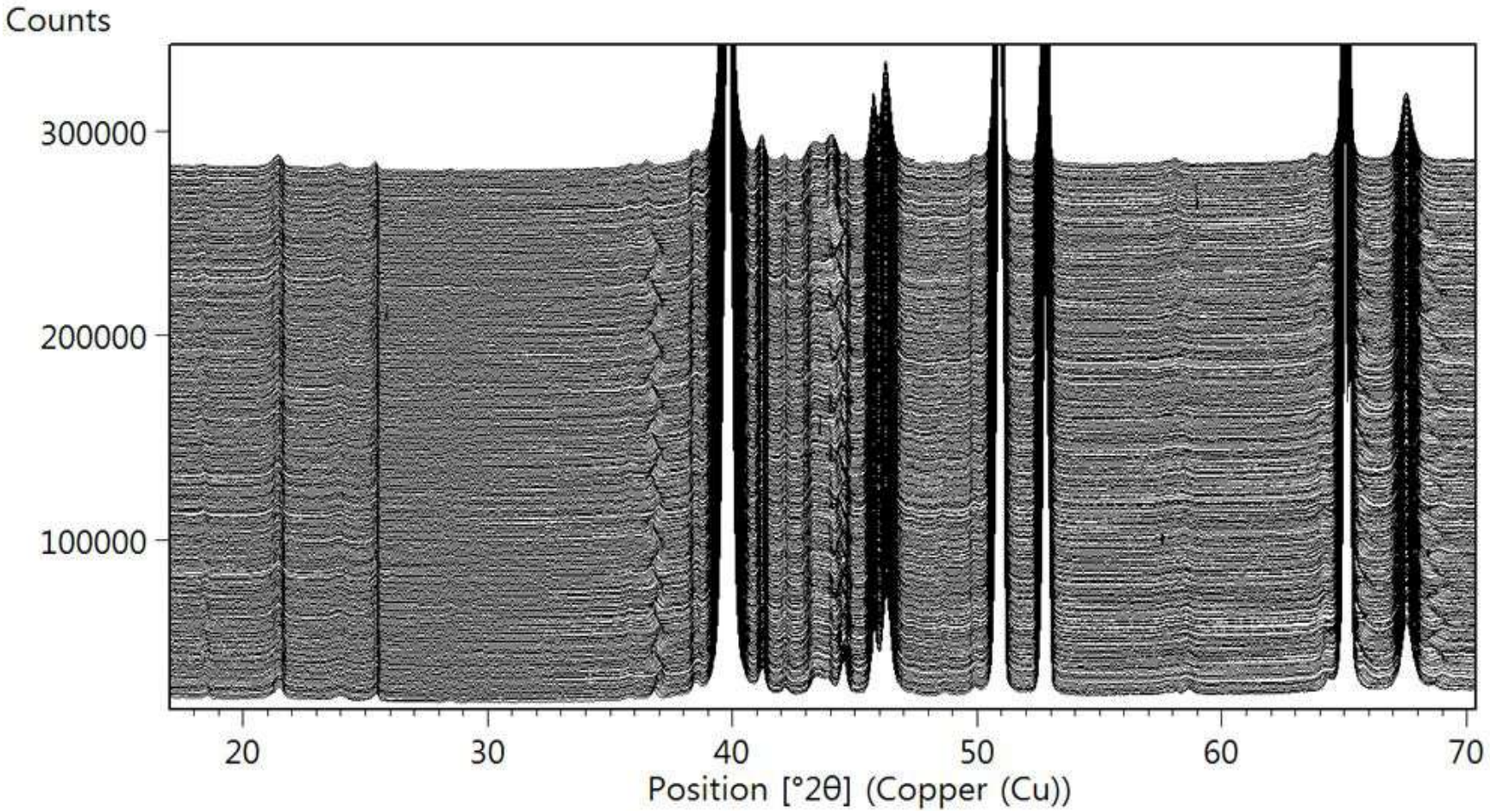
OLO ($Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$) powder had been provided by customer for the reliability of in-situ XRD system.

Sample preparation and electro-chemical test conditions are following:

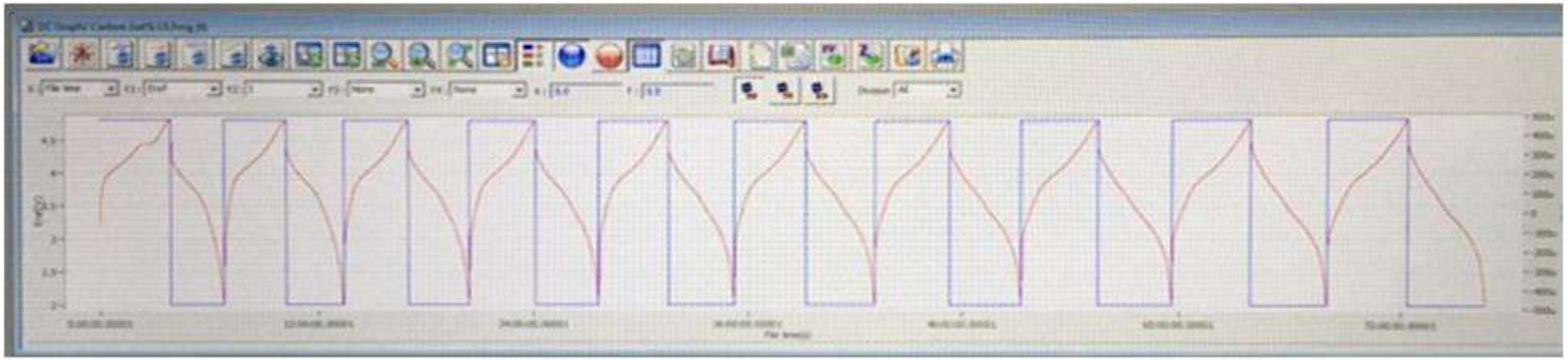
- Working electrode: OLO 80%, carbon 10% and PVdF 10% on a Aluminum foil
- Active mass : 13.7 mg
- Counter electrode: Lithium metal
- Electrolyte solution: $LiPF_6$ / EC:DMC=1:1
- Charge-discharge test:
- Curr-ent density: 0.1 C-rate
    - Voltage range: 3 ~ 4.3 V
    - # of cycle: 1 time
    - Room temperature

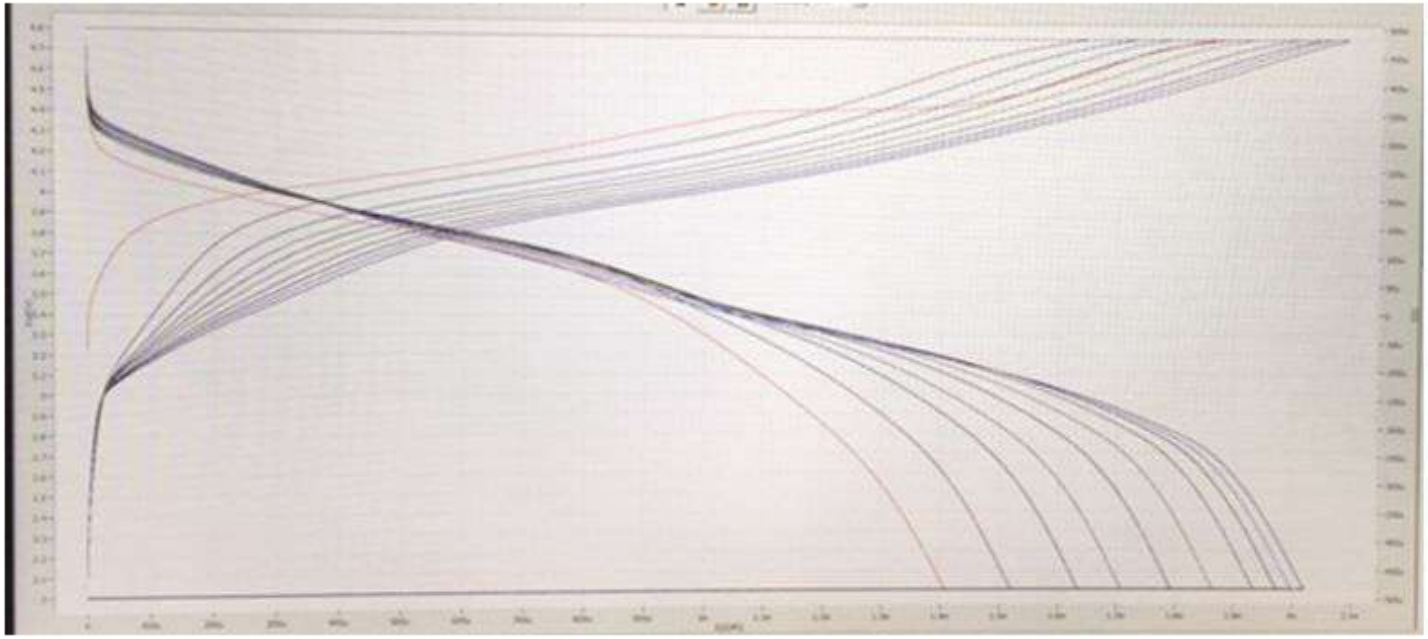
XRD test

- Cu anode / BBHD / ISBC / PIXcel
- 10 min per scan

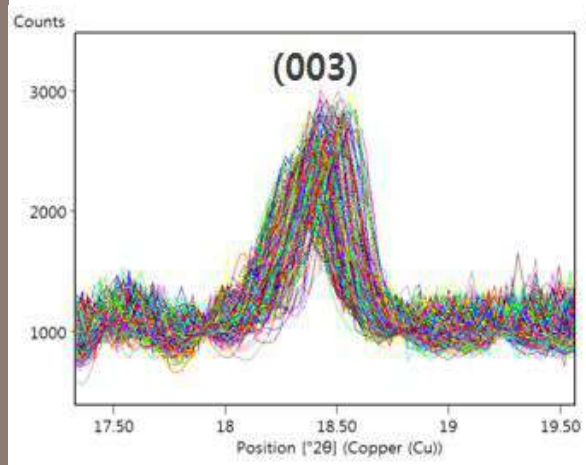


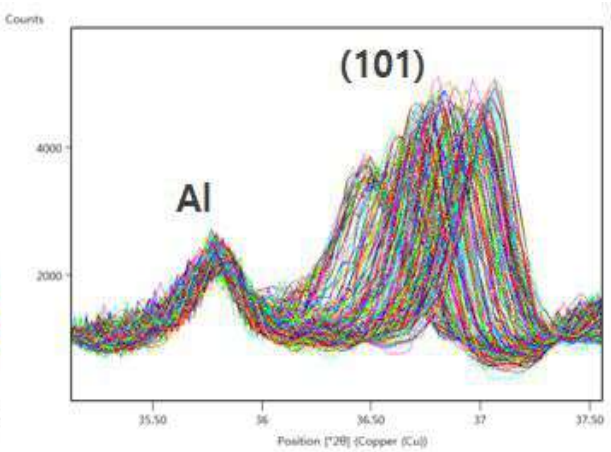
XRD DATA - EXPERIMENTAL : OLO

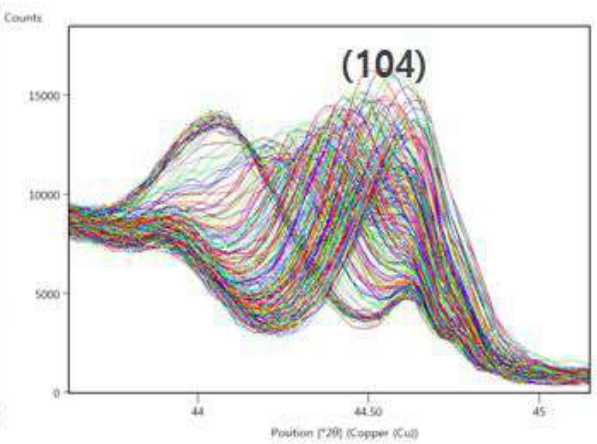


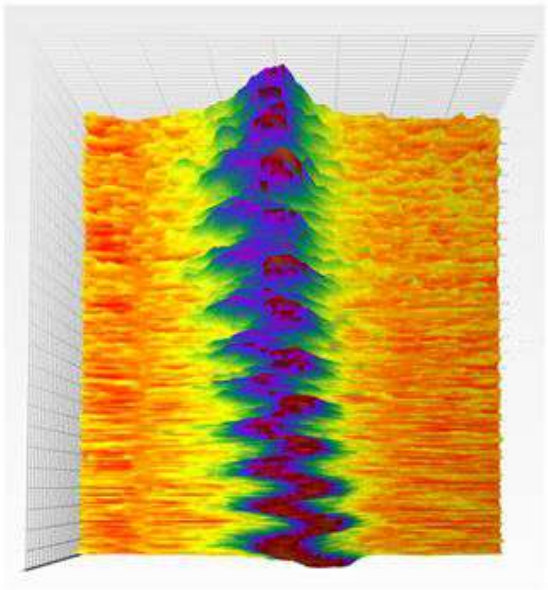


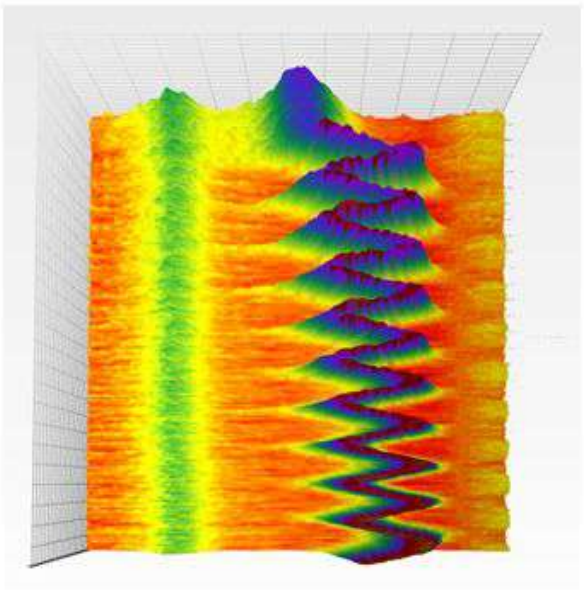
XRD DATA - EXPERIMENTAL : OLO

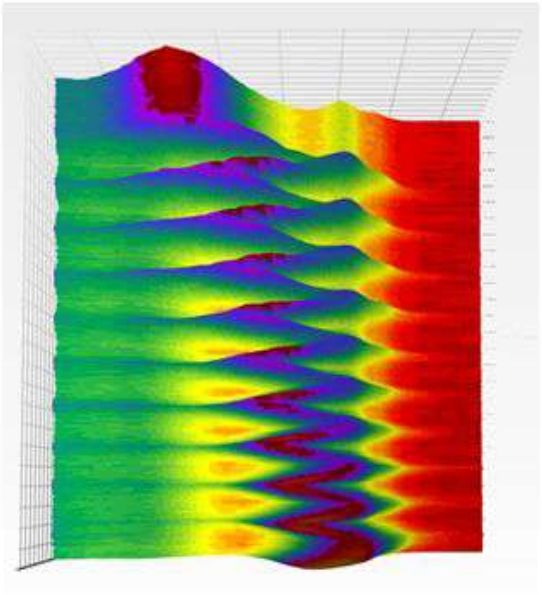

Counts
(003)
3000
2000
1000
17.50
18
18.50
19
19.50
Position [°2θ] (Copper (Cu))

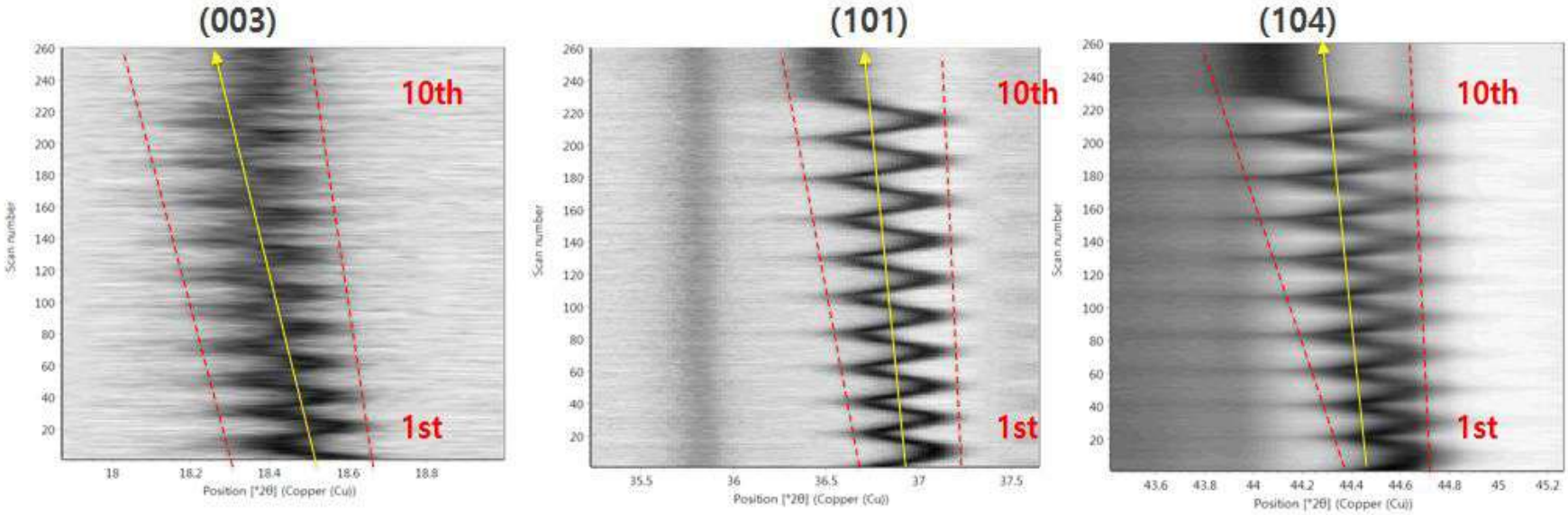

Counts
(101)
Al
4000
2000
35.50
36
36.50
37
37.50
Position [°2θ] (Copper (Cu))


Counts
(104)
15000
10000
5000
0
44
44.50
45
Position [°2θ] (Copper (Cu))









- By performing a single in-situ experiment, several hundreds of XRD profiles has been obtained. We can also find a structural behavior in real-time.

- In this test, we could see that average volume of unit cell is increasing, and also cell capacity is getting larger by repeating charge-discharge cycles. On the other hands, supporting materials has kept their peak position. (it should be)

XRD DATA - EXPERIMENTAL : OLO

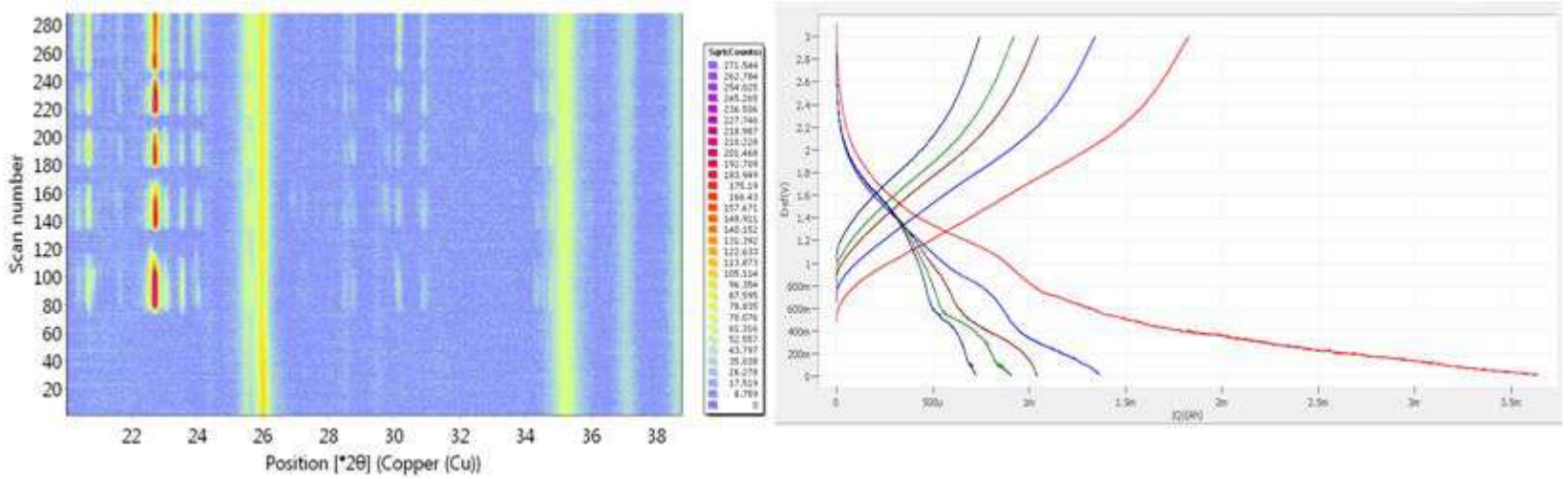
NbO2 powder had been provided by customer for the reliability of in-situ XRD system.

Sample preparation and electro-chemical test conditions are following:

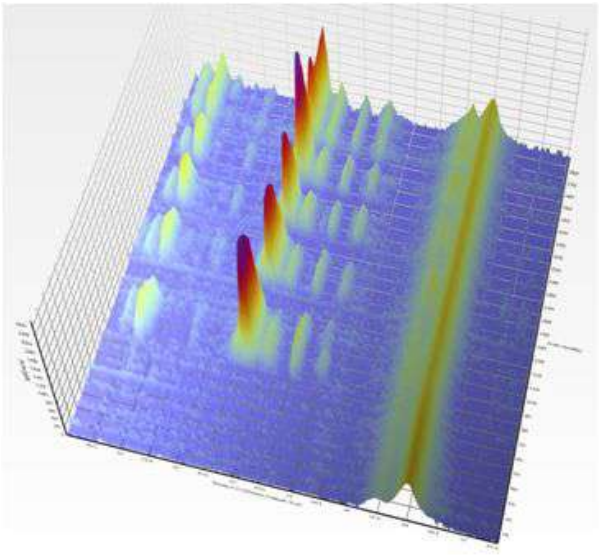
- Working electrode: NbO2 70%, carbon 10% and PVdF 20% on a Special metal foil
- Active mass : 0.02164 g
- Counter electrode: Lithium metal
- Electrolyte solution: $LiPF_6$ / EC:DMC
- Charge-discharge test:
- Curr-ent density: 0.1 C-rate
    - Voltage range: 0 ~ 3 V
    - # of cycle: 5 time
    - Room temperature

XRD test

- Cu anode / BBHD / ISBC / PIXcel
- 10 min per scan
- Designed to 120 scans per cycle



- XRD patterns were dynamically changed during de-, intercalation process of the Li ion into the working electrode.



- We believe that NbO_2 was decomposed to Li_xO_y and Nb_xO_y during discharge process except 1st cycle. However, it is not yet revealed what the mechanism is. Because, this is never published in battery journals.

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a spectris company

Augment Your Battery Research With Non-Ambient In Operando XRD

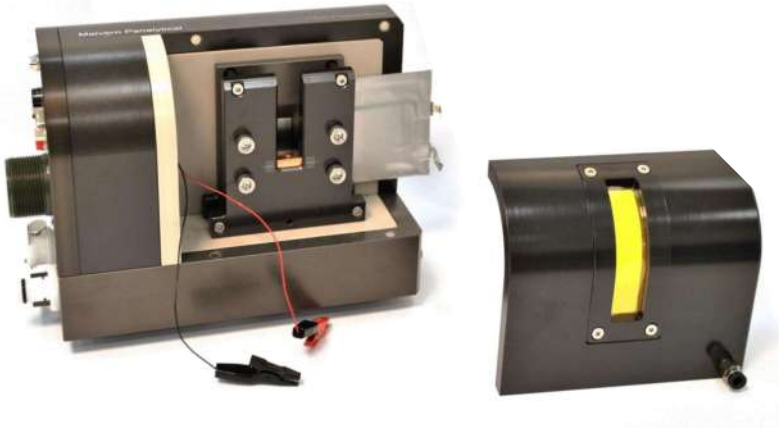
Z. Bao, M. Gateshki, M. Sommariva, A. Kumar, D. Lee, S. Speakman, U. Tiwari
17 August 2022
Malvern Panalytical, The Netherlands

VTEC and VTEC-trans for temperature

VTEC (variable temperature electrochemical cell)

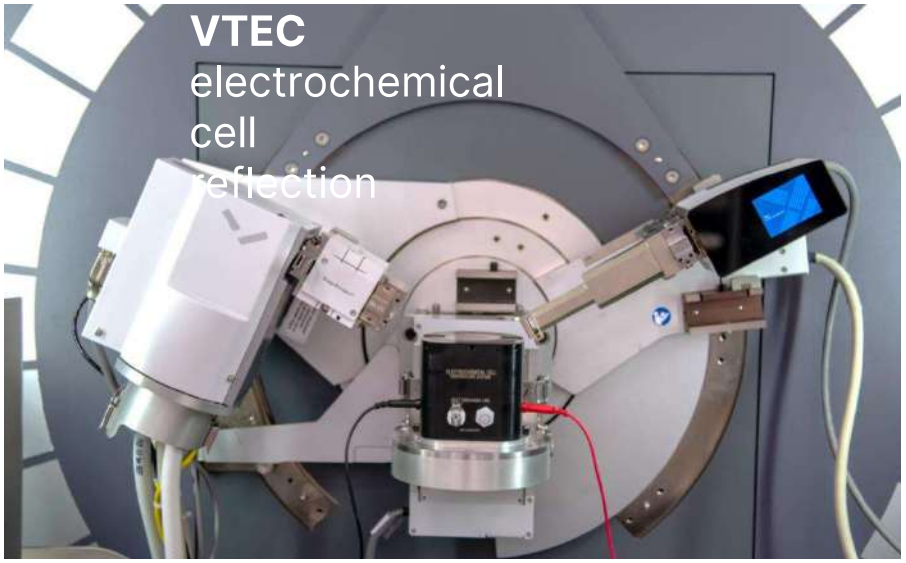
VTEC-trans
Pouch cell
Transmissio
n

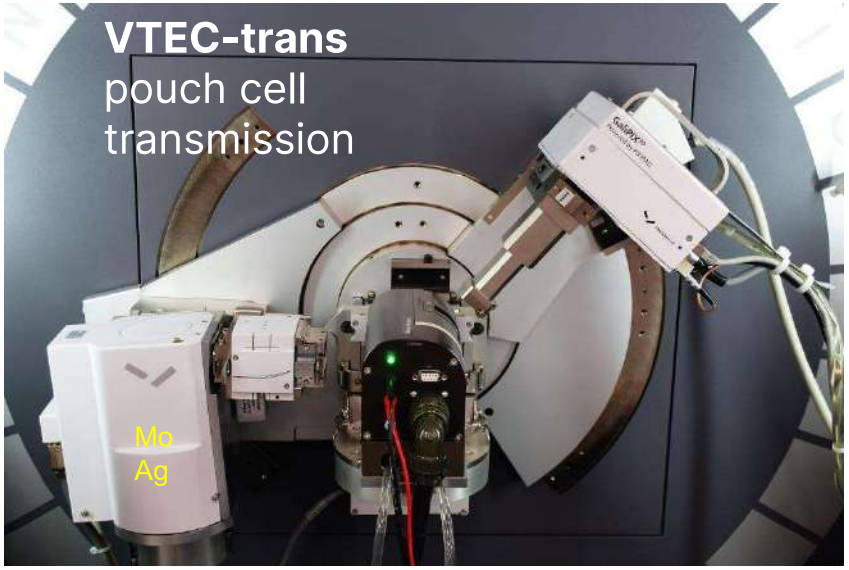
VTEC
Electrochemical cell
Reflection geometry



in operando & *in situ* study

VTEC and VTEC-trans integrated stages





GaliPIX^{3D} Detector with CdTe sensor

~ 100% QE for Ag, Mo, Cu radiation

Temperature range:

trans)

2 – 140° (VTEC)

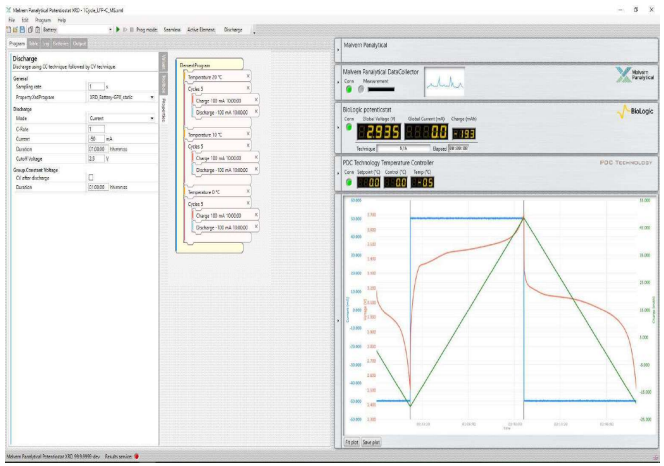
Fully integrated SW control with BioLogic potentiostat*

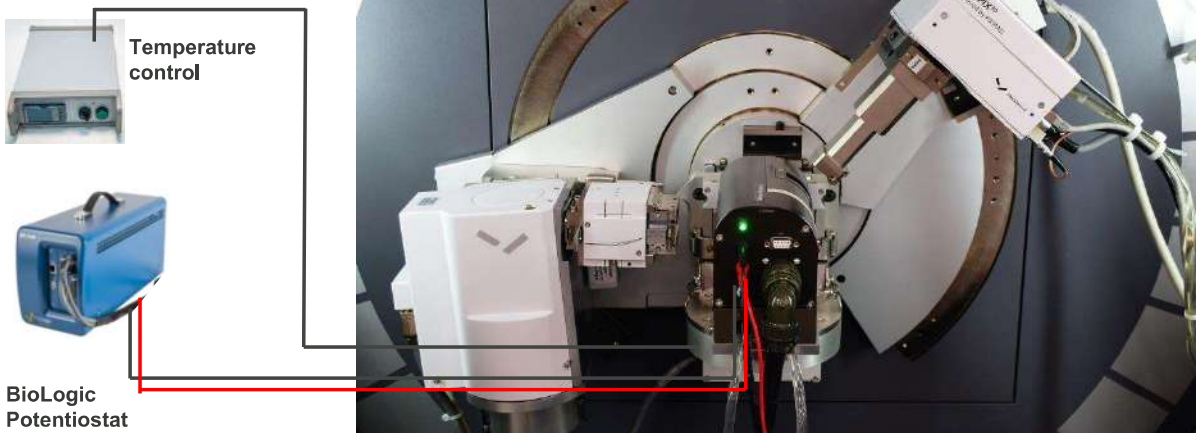
- **Potentiostat**
- **Temperature unit**
- **Empyrean XRD system**

- Other brands can be supported:
  - Maccor, IVIUM, Lanhe/Lande.
- Others on request

in operando & *in situ* study

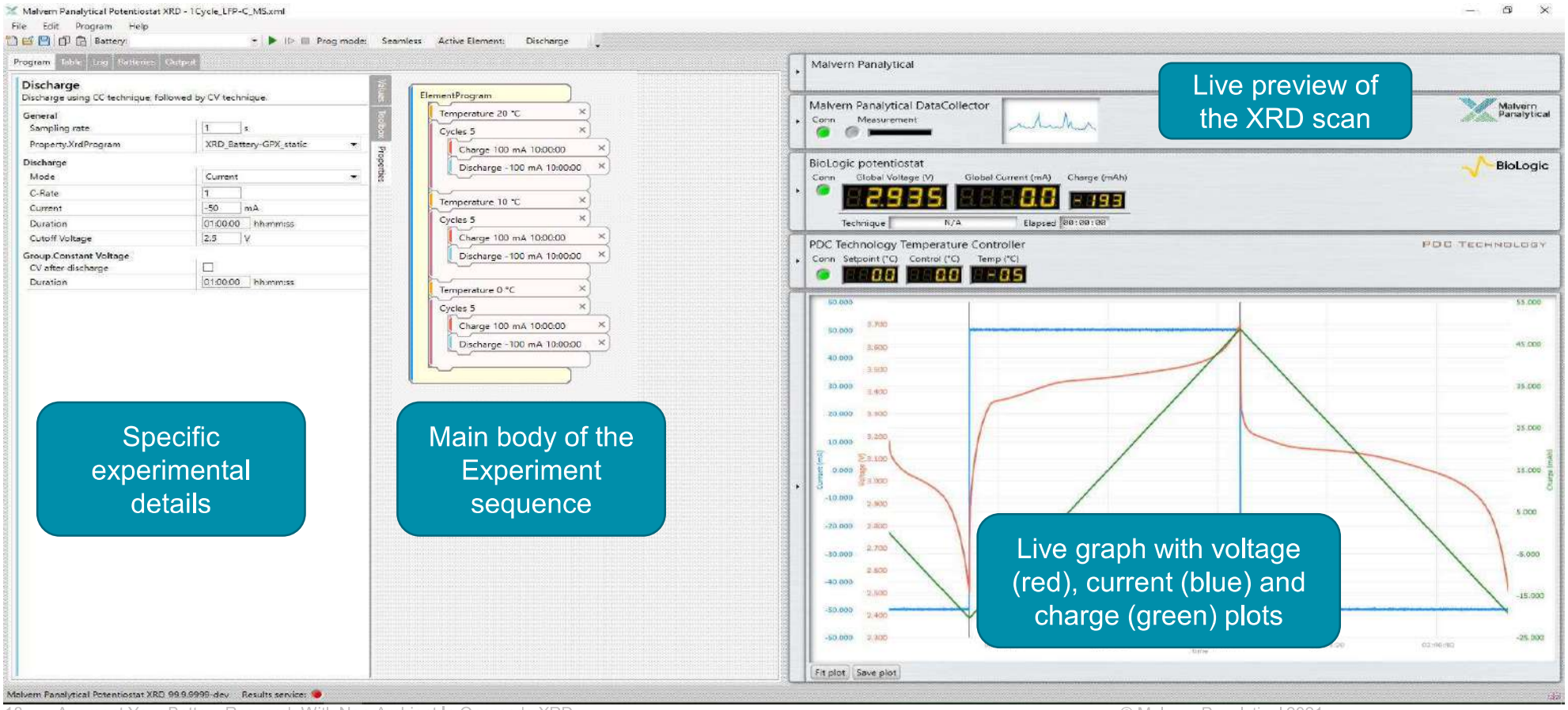
How does it work





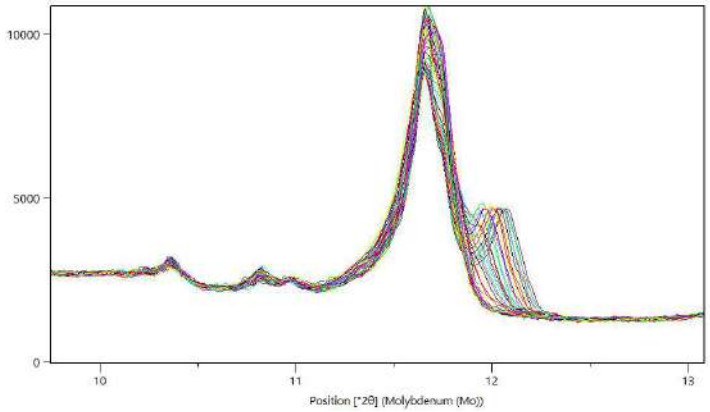
in operando & *in situ* study

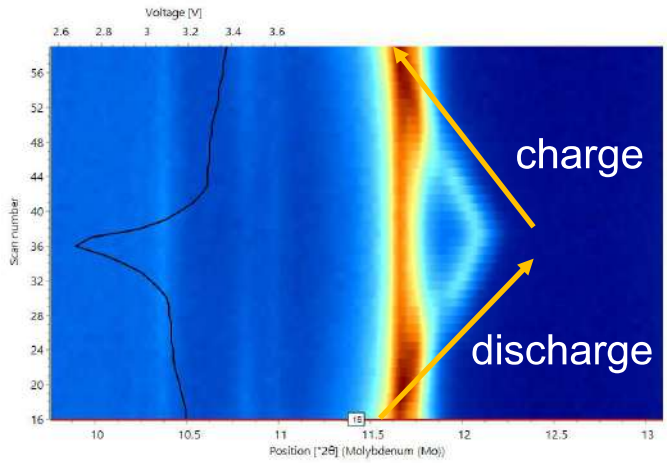
Fully synchronized control software



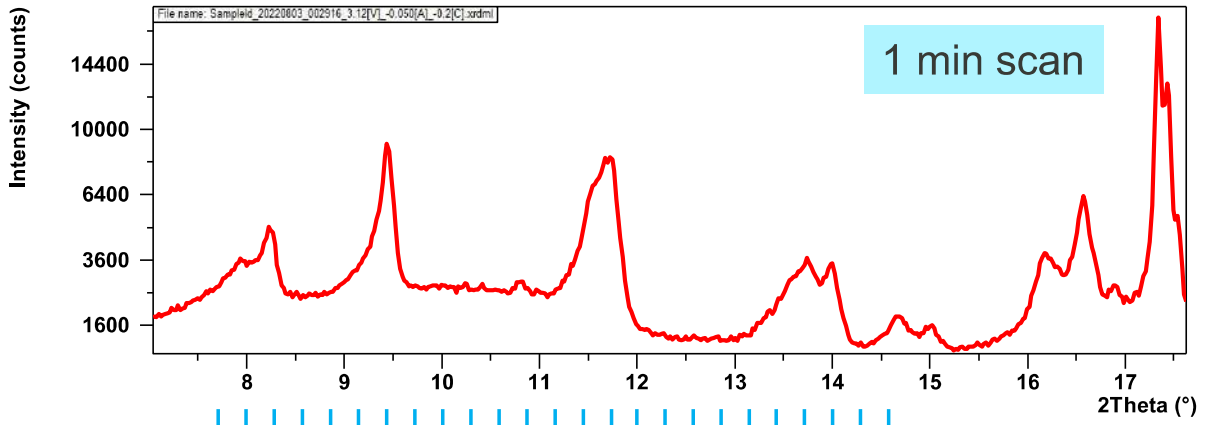
How does it work

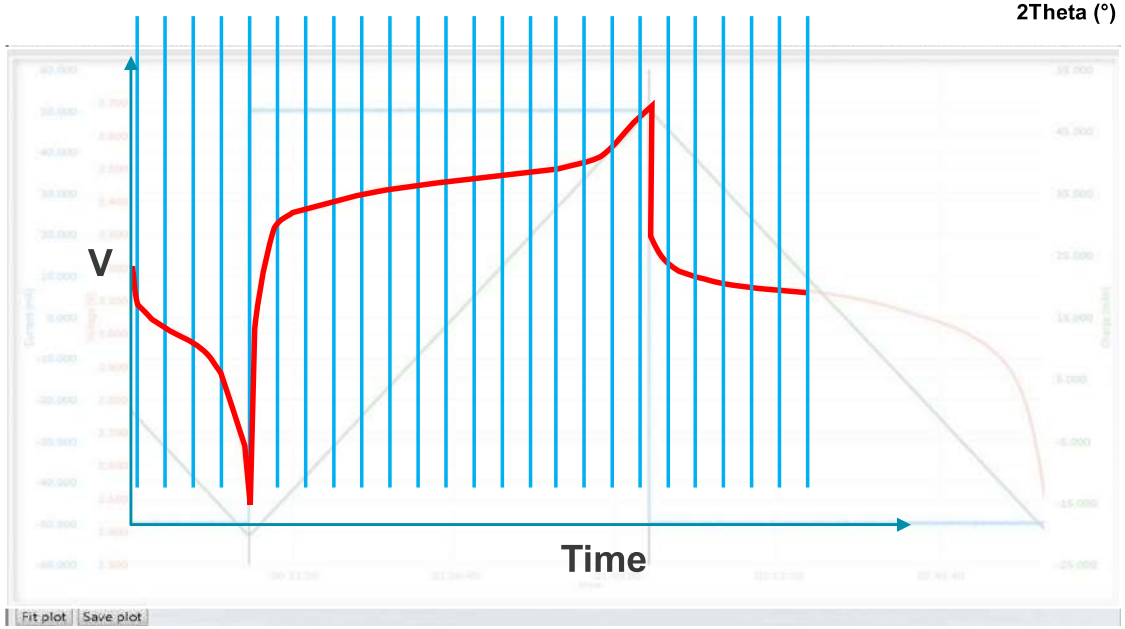
Data Collection methods





Malvern

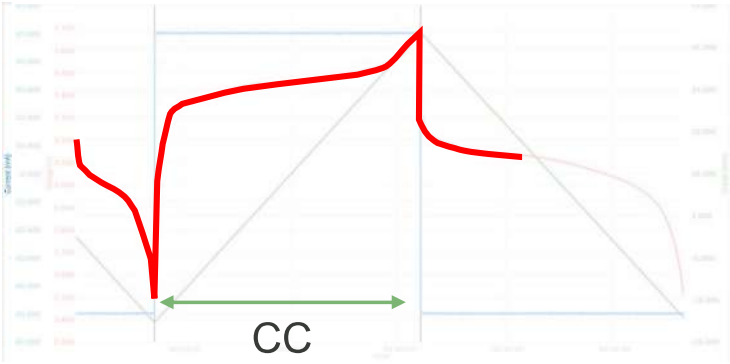




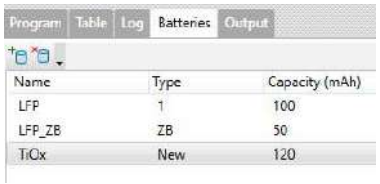
Advanced measurements

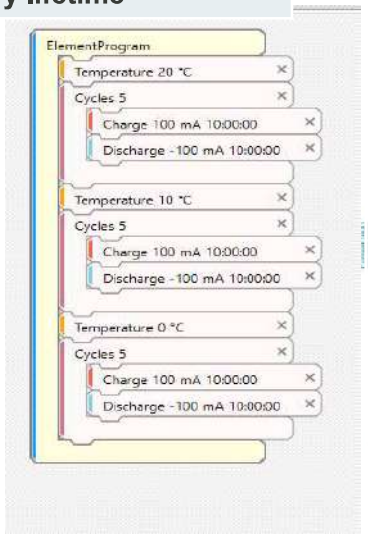
Integrated solutions for productivity and flexibility

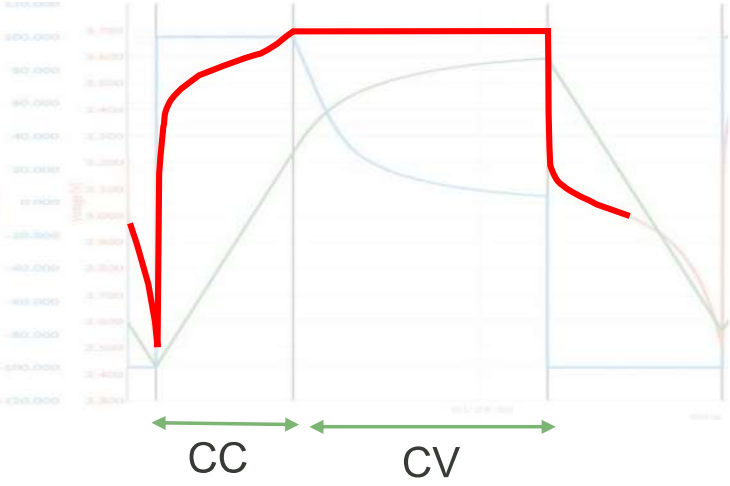
Method	Advantage	Disadvantage
Constant Current (CC)	Easy to implement	Low capacity utilization
Constant Voltage (CV)	Easy to implement	Lattice collapse
Constant Current Constant Voltage (CC-CV)	• High capacity utilization • Stable terminal voltage	Could be difficult to optimize the best charging speed, energy loss, temperature variation
Multi-Stage Constant Current (MCC)	• Easy to implement • Fast Charging	Could be difficult to optimize the best charging speed, capacity utilization, battery lifetime



- Convenient feature
  - Define user batteries library
  - C-rate or mA
  - Drag and drop
  - Flexible XRD measurement programs
  - Loop/cycle setting
  - Temperature setting
    - ramping measurement too
- Safety setting
  - Set cut-off current/voltage
  - Set battery Voltage and Capacity

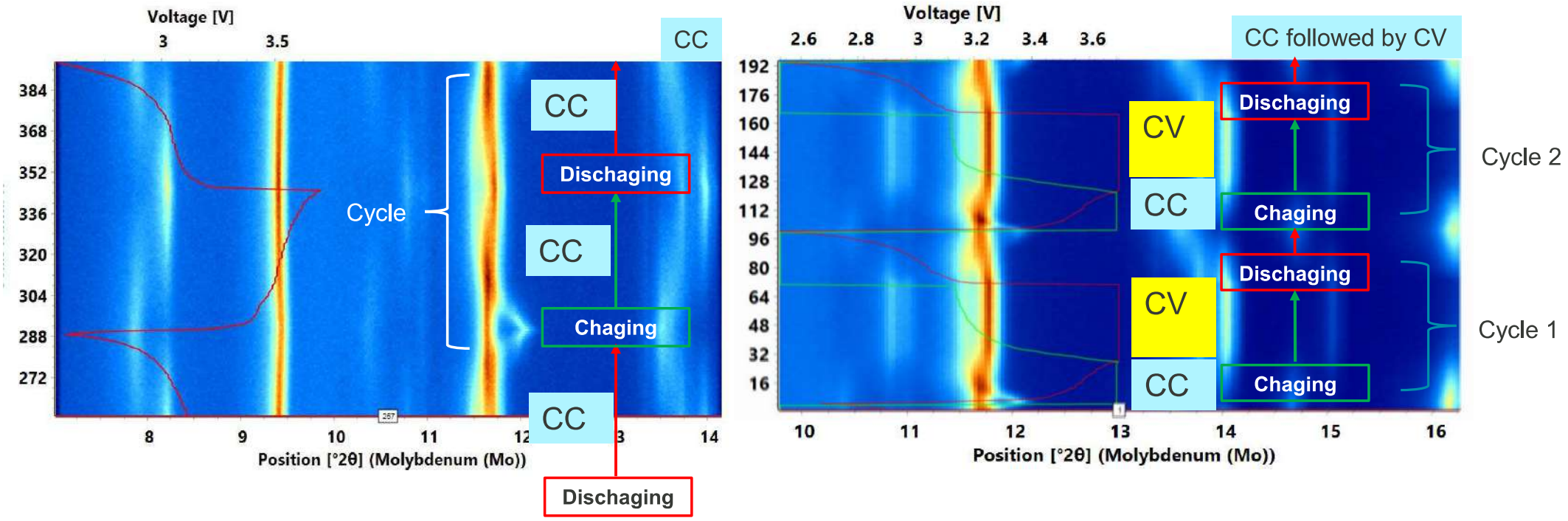






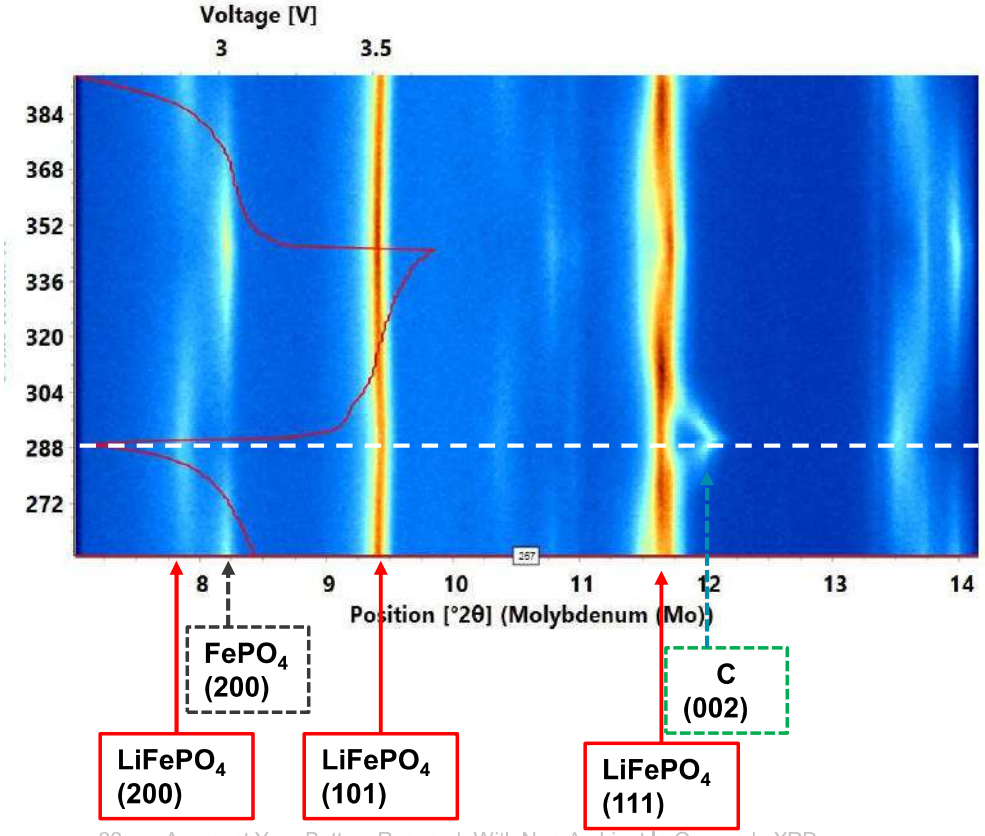
Example: *in operando* measurements

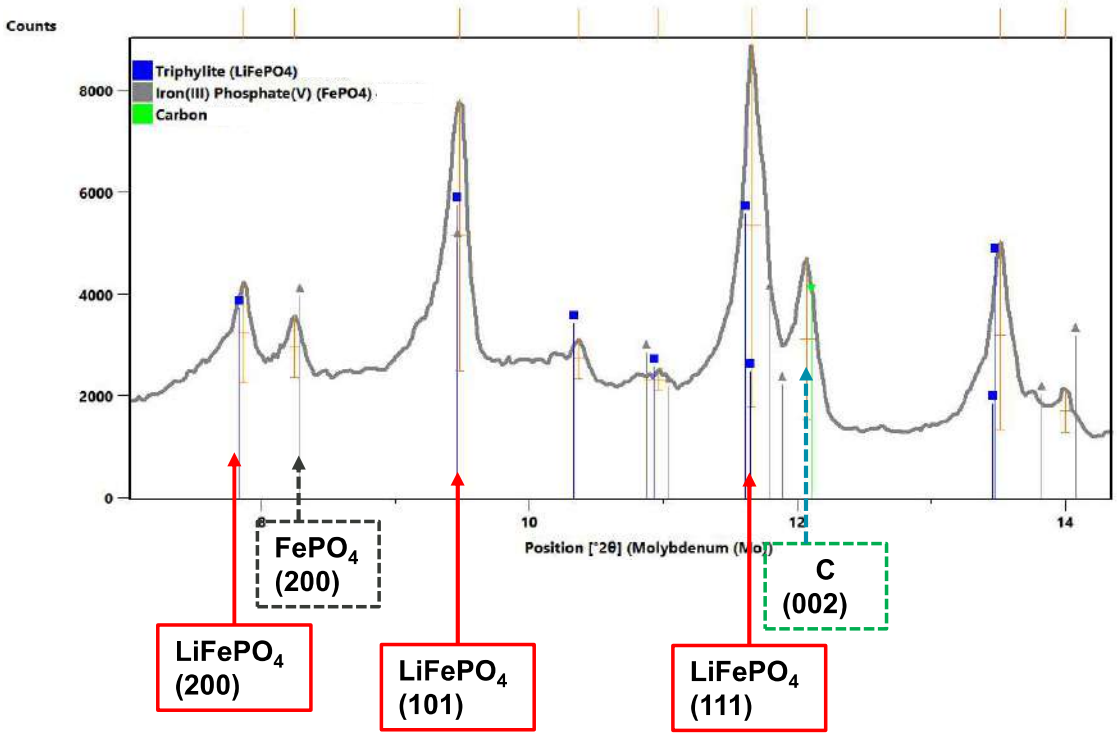
Battery: LFP charge/discharge at 0.5C (50 mAh)



Understand the phase change

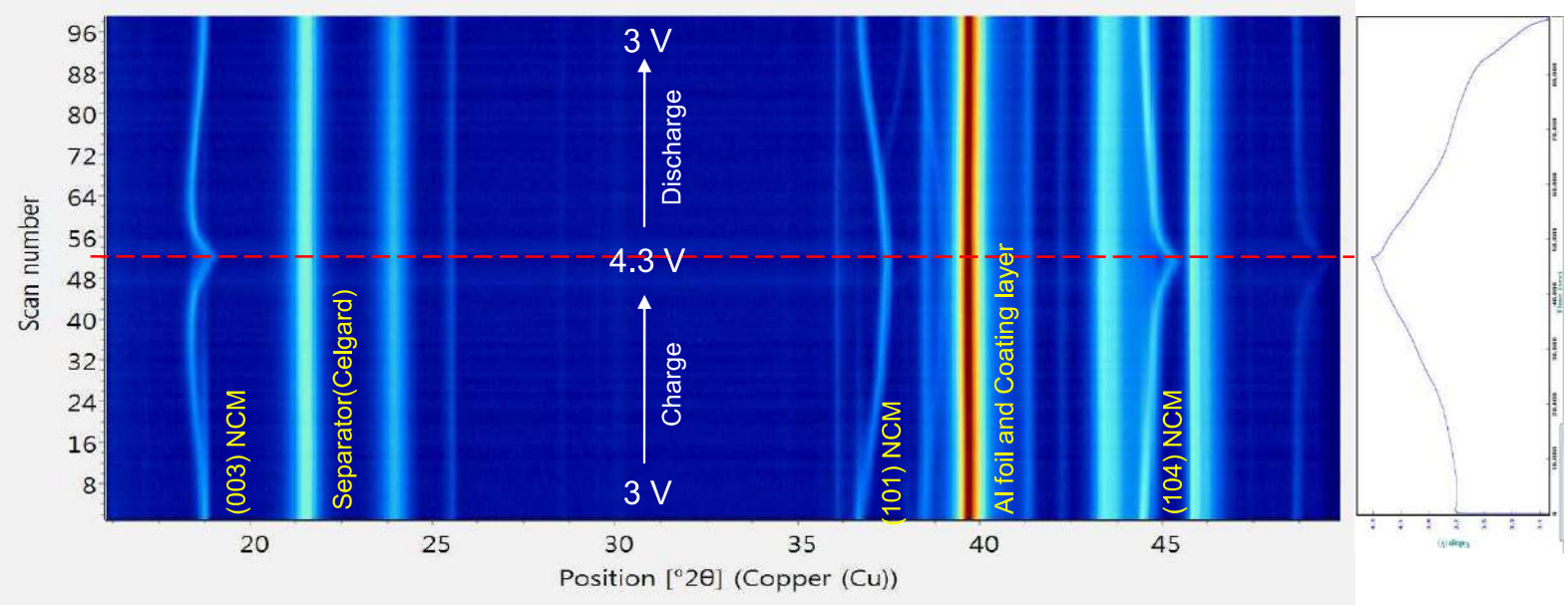
Battery: LFP charge/discharge at 0.5C (50 mAh)

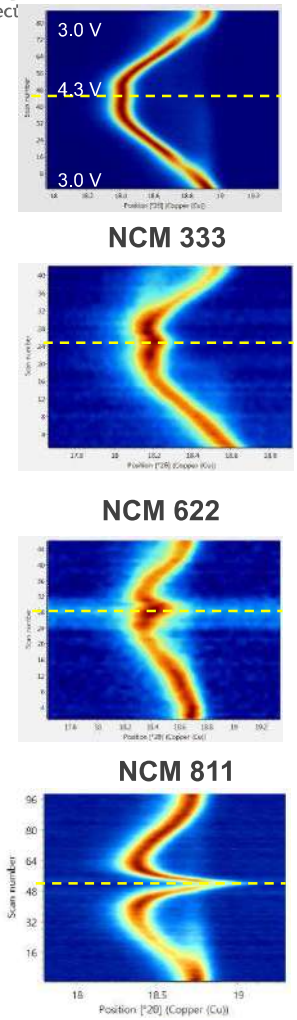




Example: cathode composition effect

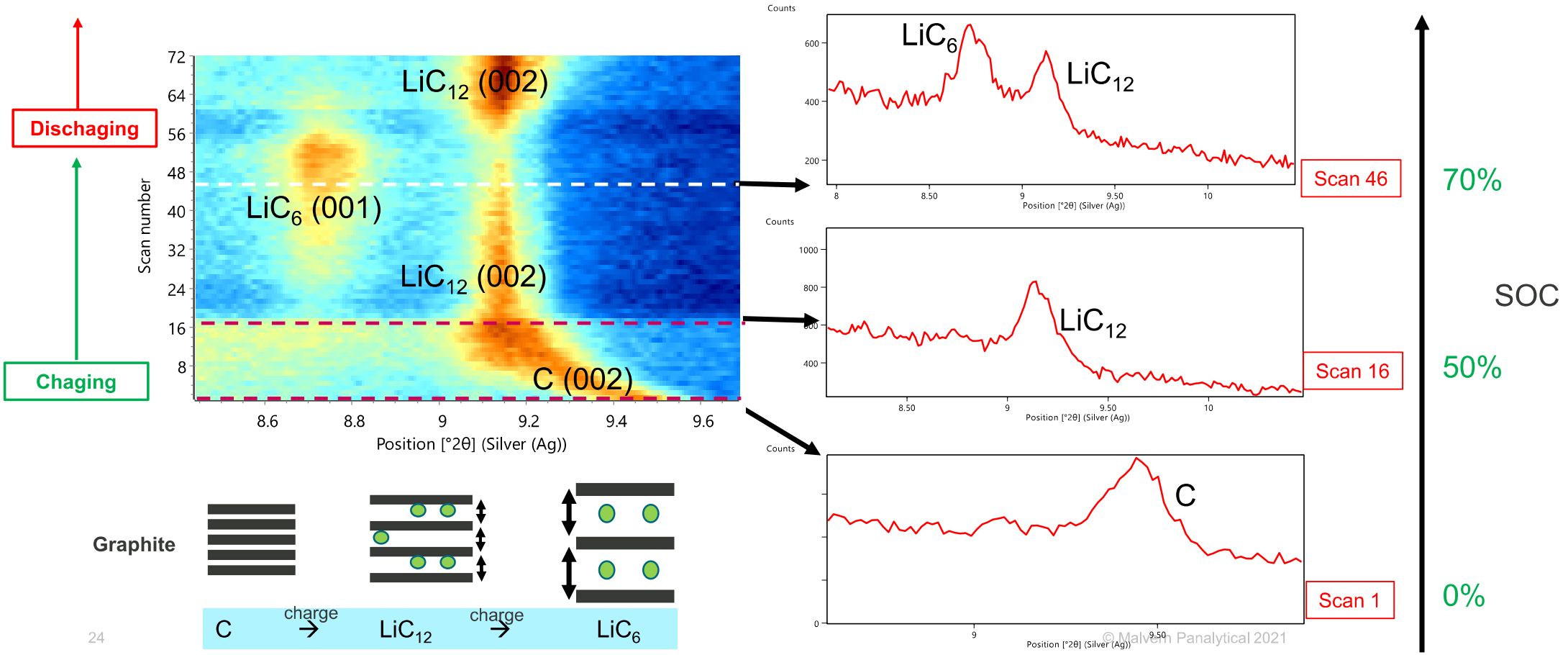
Battery: LCO, NCMs at 0.1 C-rate





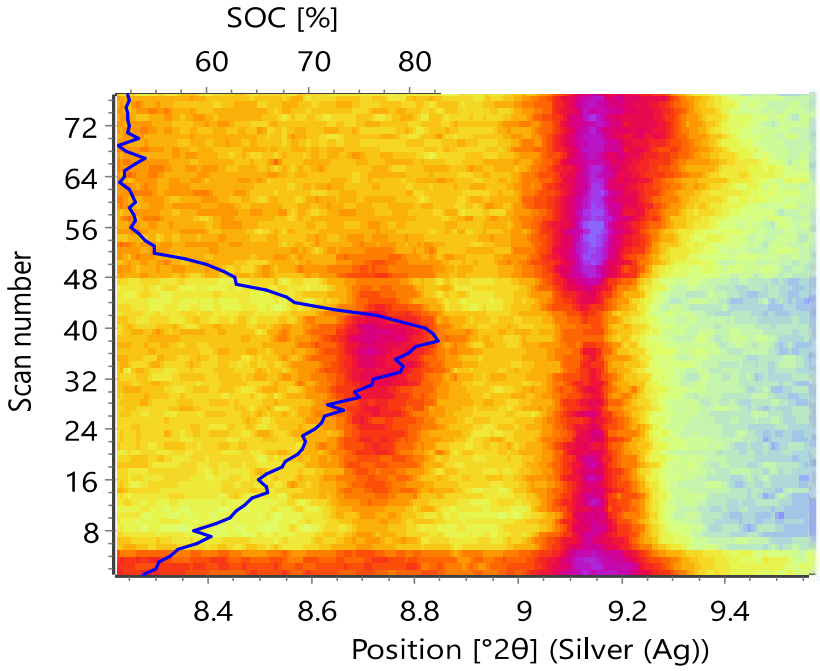
Example: state of charge vs. crystalline phase

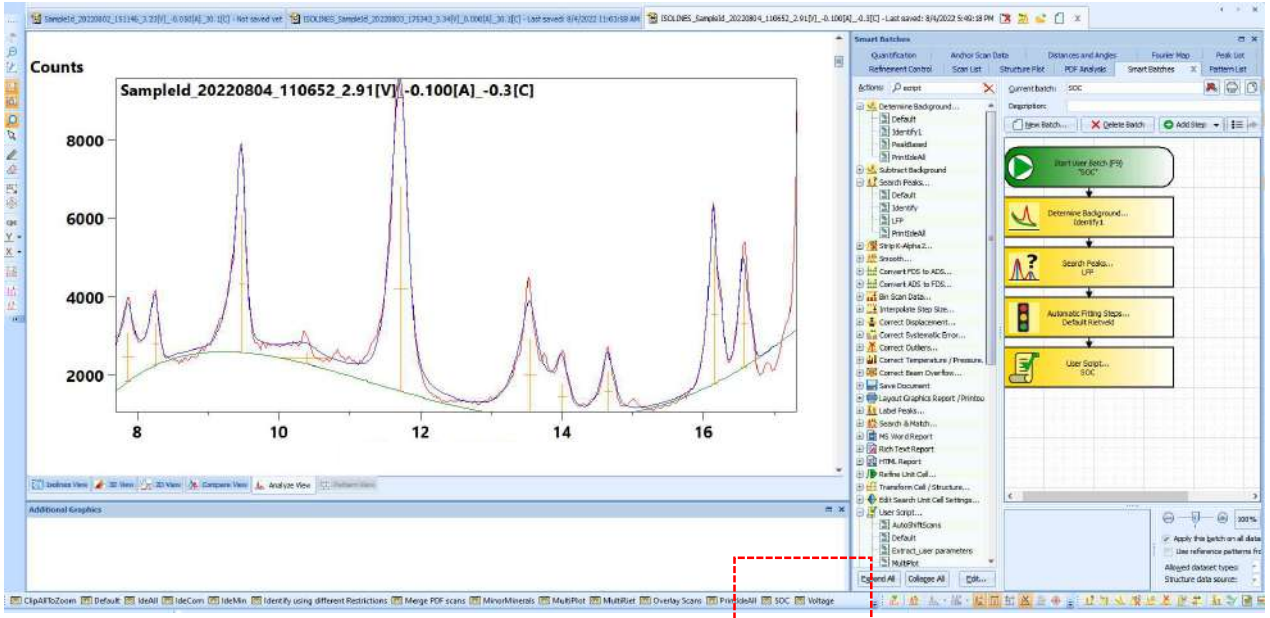
Battery LCO, Areas of the anode peaks

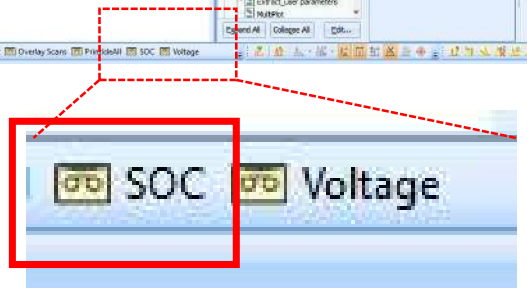


Data Analysis with HighScore Plus SW

Automated data processing

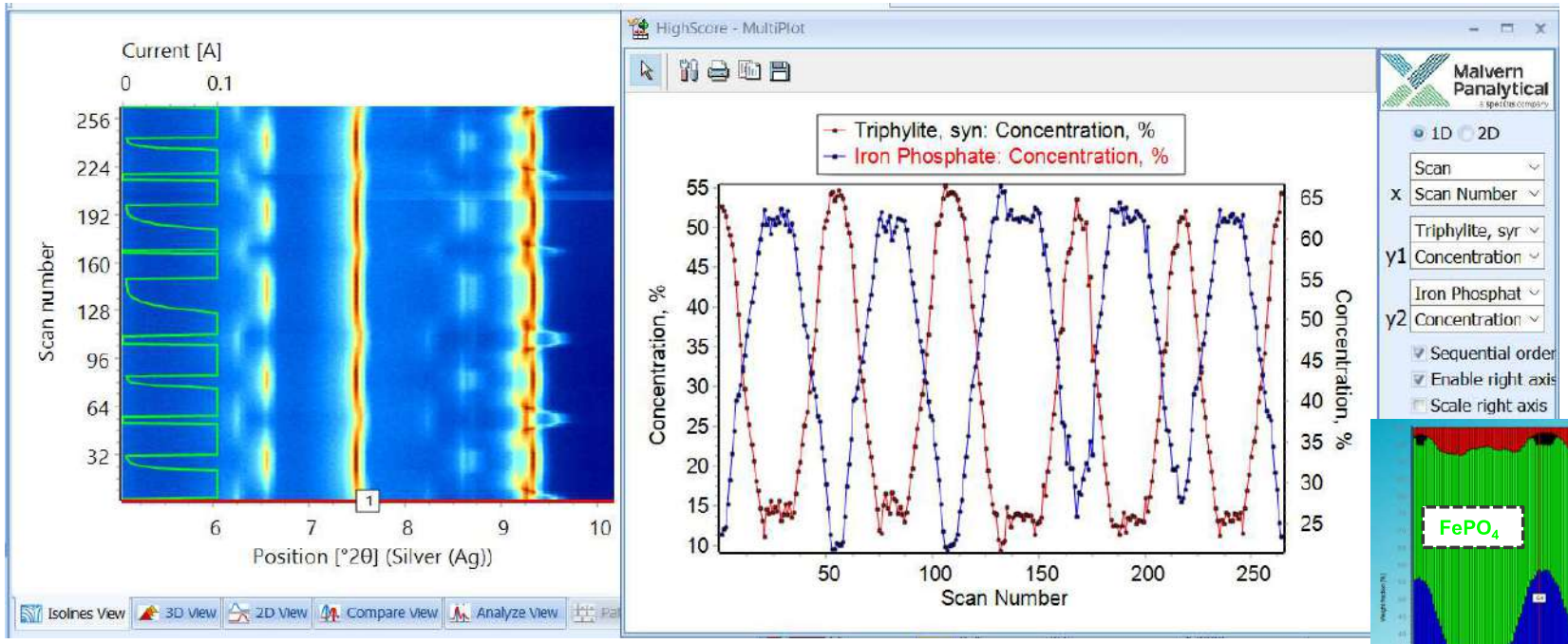




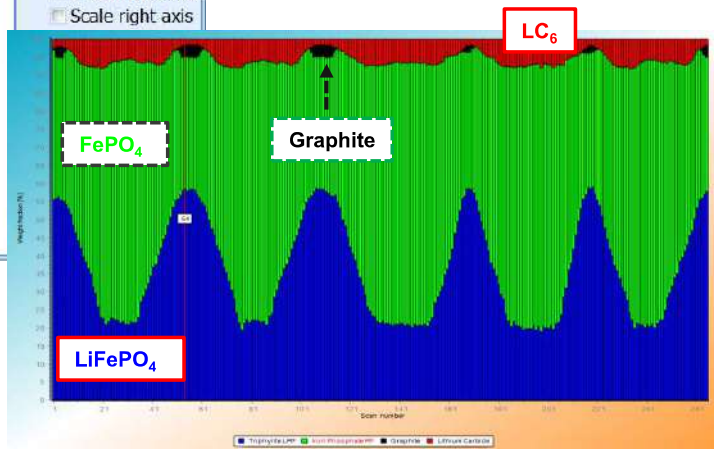


Automated quantification analysis

HighScore Plus: specific features for batteries

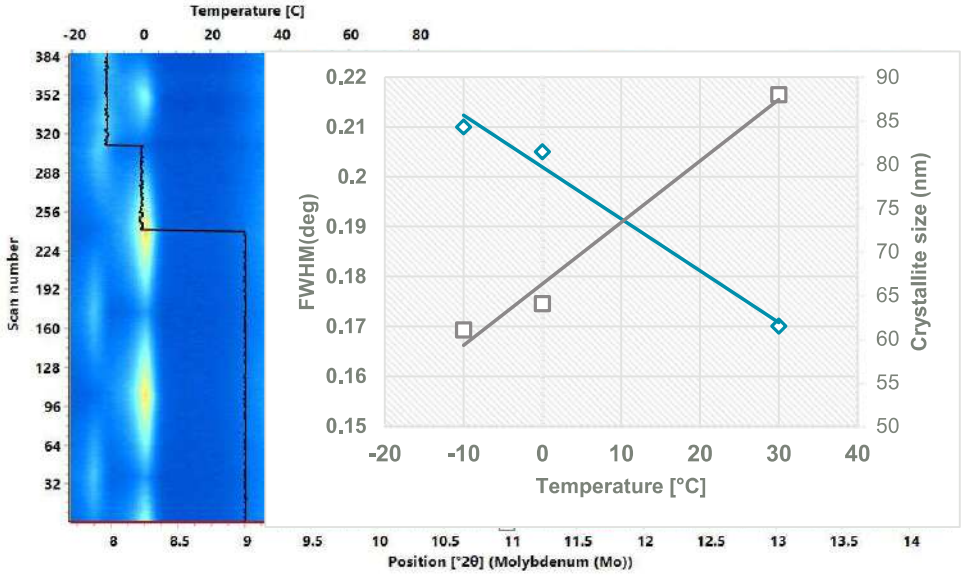


MultiPlot tool:
for quick and easy visualization of global (voltage, current, temperature) and refined parameters (weight percentage, lattice parameters…)

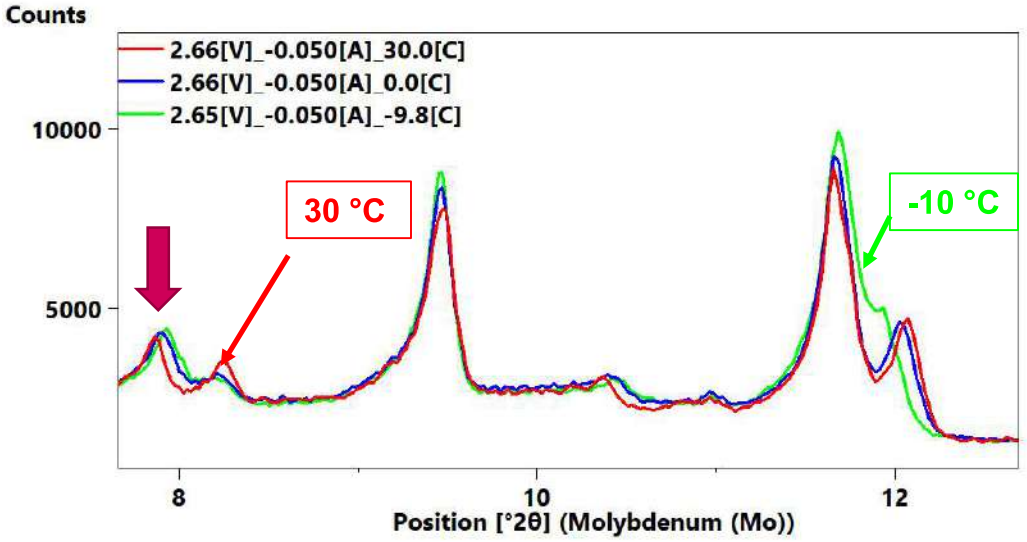


In operando at different temperatures

Why it's important to understand the temperature effect?



$LiFePO_4$ battery cycled at different temperatures



- Clear temperature dependent effect
  - **Thermal expansion**
  - **Higher delithiation rate at 30°C (intensity)**
  - **Crystalline defects (peak width)**

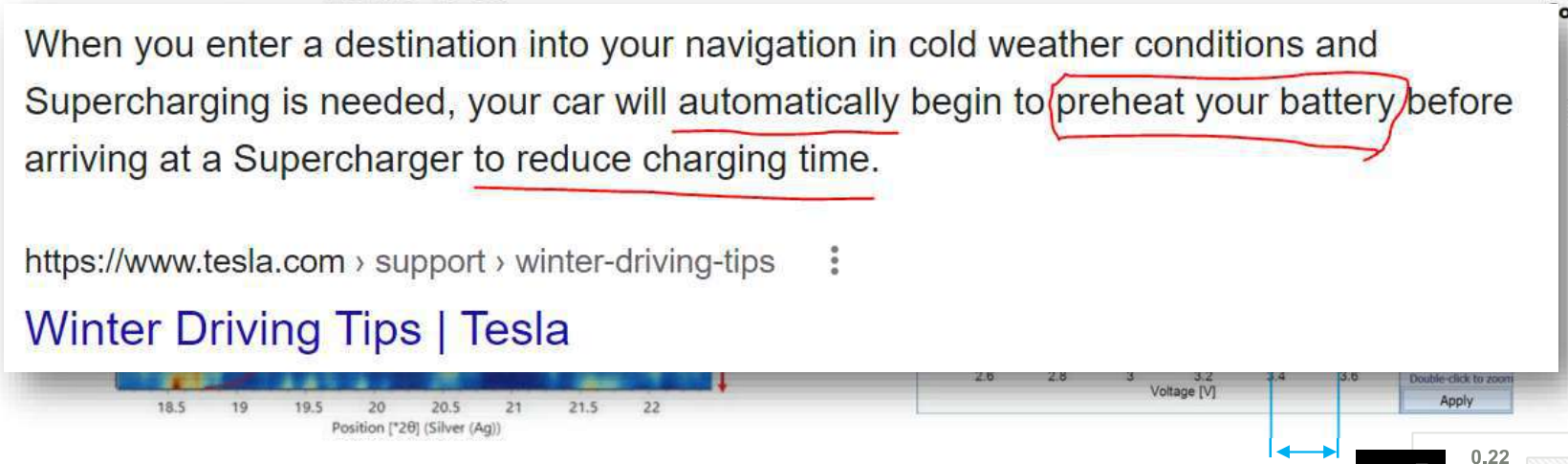
Temperature Controlled Battery Solutions

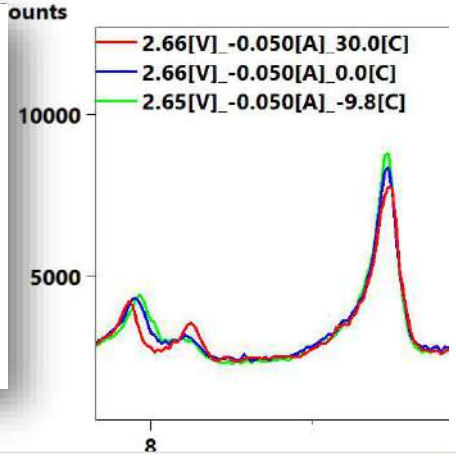
Cold weather performance of electric vehicles is a challenge – but why?

When you enter a destination into your navigation in cold weather conditions and Supercharging is needed, your car will automatically begin to preheat your battery before arriving at a Supercharger to reduce charging time.

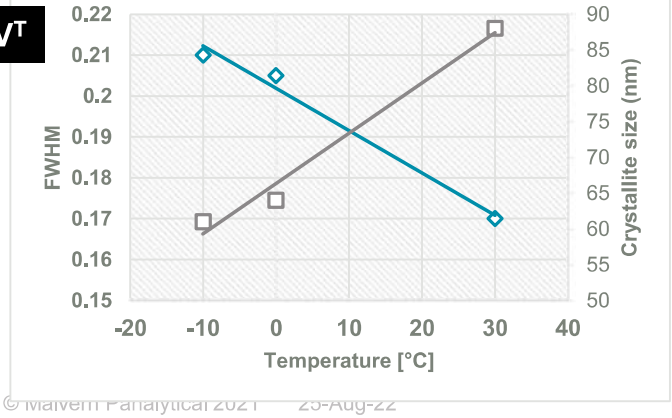
https://www.tesla.com › support › winter-driving-tips

Winter Driving Tips | Tesla





ΔV^T



- ΔV^T ➔ temperature dependent charging/discharging characteristics.

AND……..

- Key information for evaluating the battery performance in real environment.

Conclusions

VTEC & VTEC-trans on the Empyrean XRD system

- Dedicated battery research solutions allowing the best synergy amongst the potentiostat, temperature control, and the Empyrean XRD system.
- Drag and drop SW for instrument control and the HighScore Plus analytical SW.
- The new temperature controlled, -10 – 70°C, electrochemical cells
  - VTEC for reflection geometry
  - VTEC-trans for transmission geometry
- Ready to bring the battery research to a new level.

Thank you for your attention!

www.malvernpanalytical.com