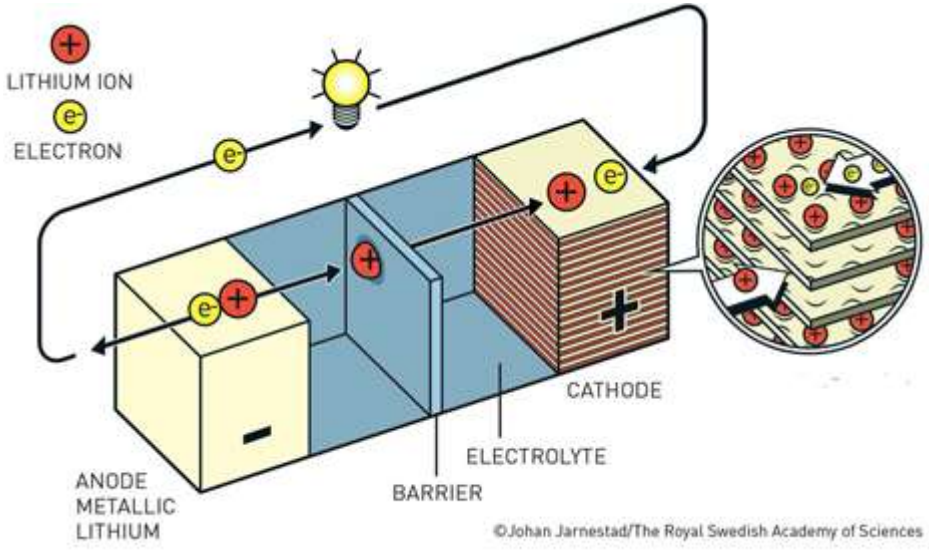
Mechanical milling effect on structural and electrochemical properties of $LiNi_xMn_yCo_zO_2$ cathode materials



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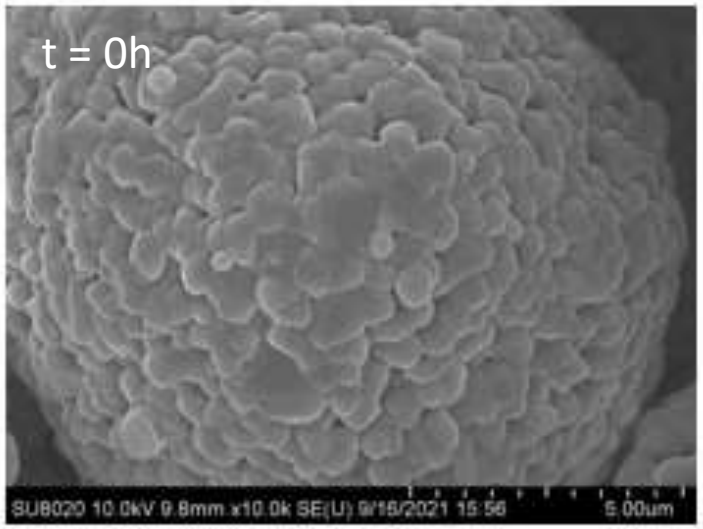
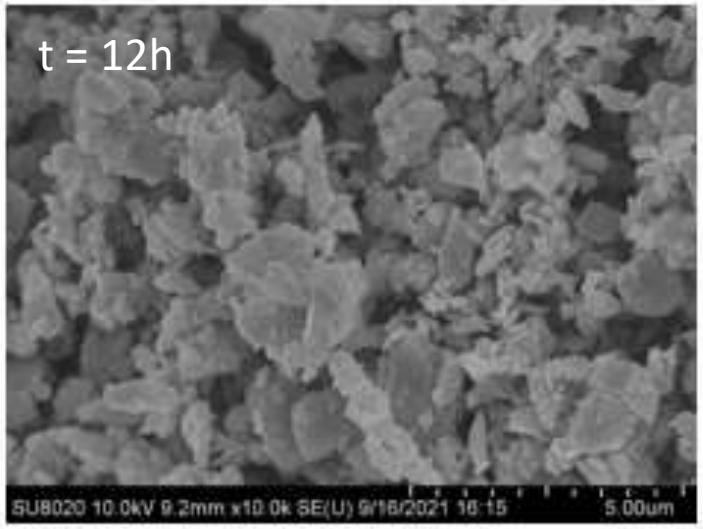
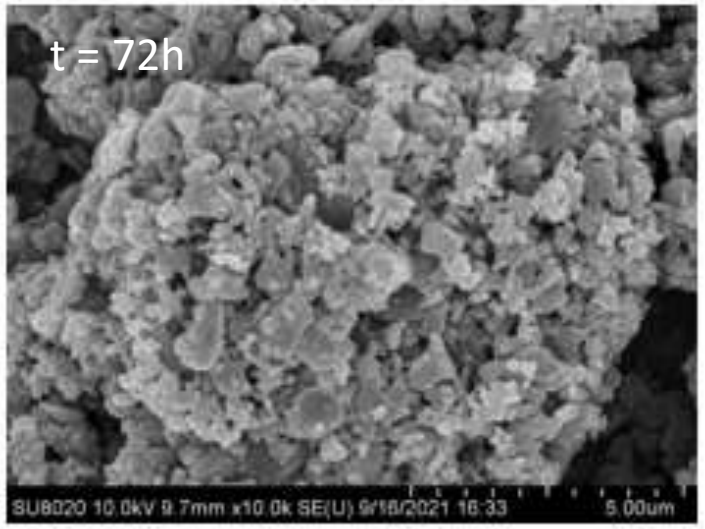
SEM images of samples before and after grinding. Received Diffraction spectra.

Powders $LiNi_xMn_yCo_zO_2$ with $x:y:z = 1:1:1; 5:3:2; 8:1:1$ are being investigated.

Each of them was milled for t = 4.5, 12, 24 and 72 hours in a planetary mill at 660 rpm.



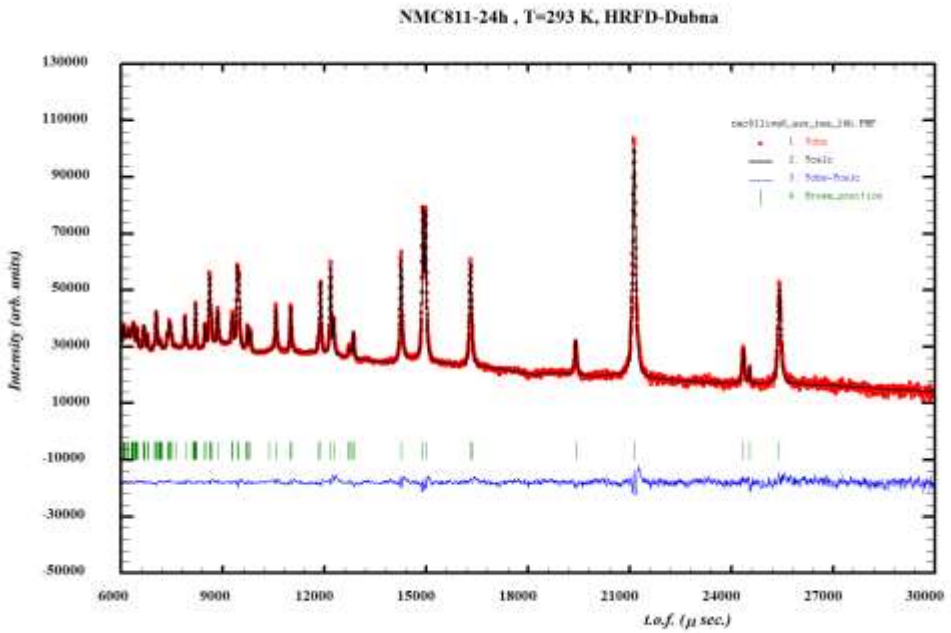


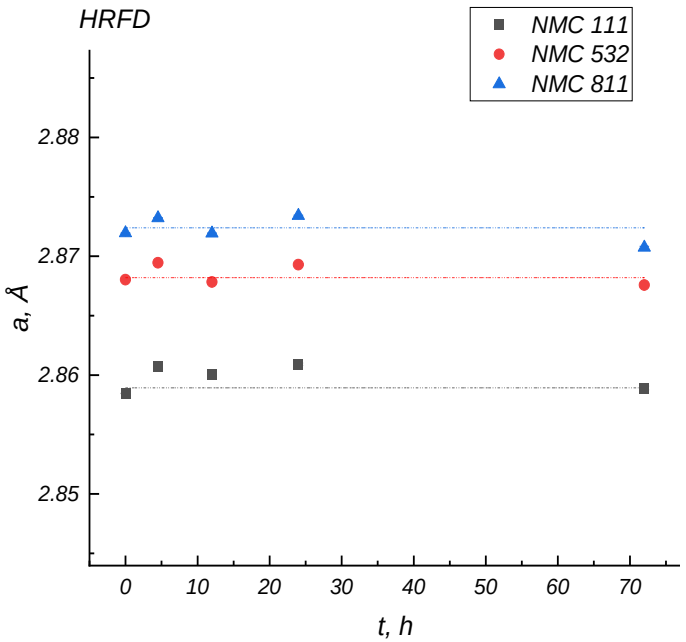


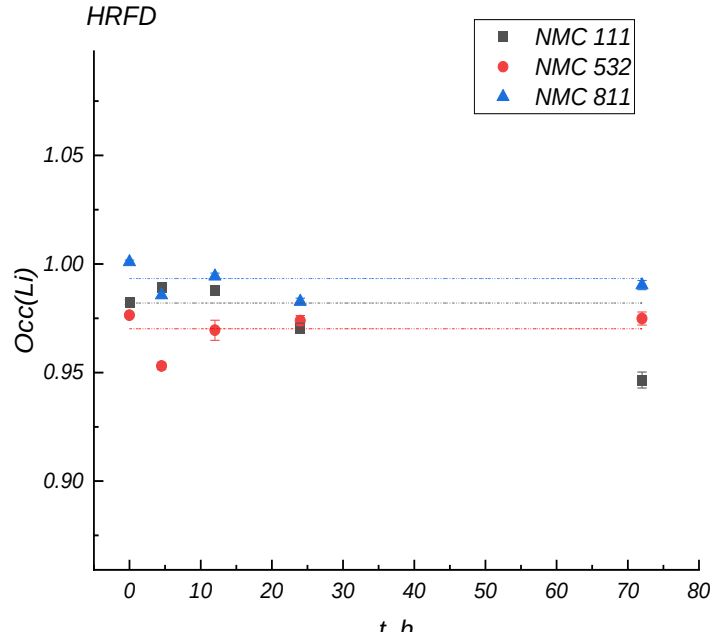
Fromboids' destruction occurs during grinding but sizes of crystallites cannot be estimated from SEM data.

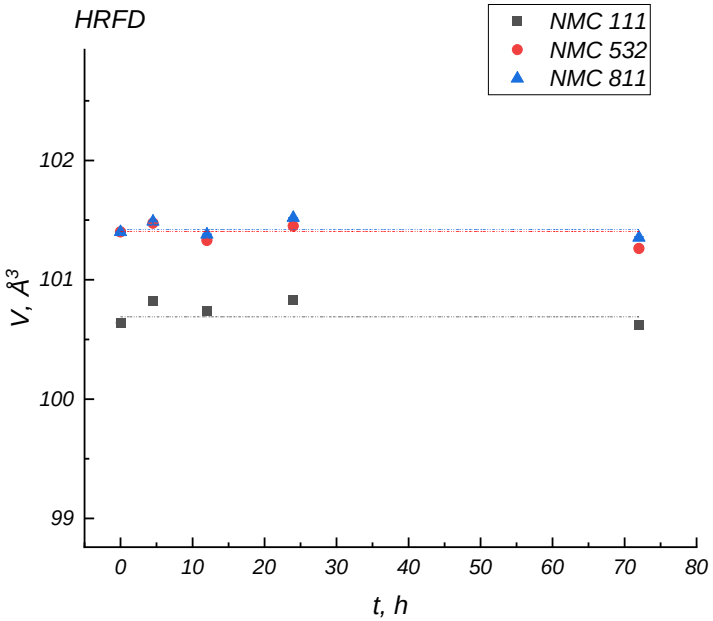
NMC 111	*pure*	*4.5 h*	*12 h*	*24 h*	*72 h*	*NMC 532*	*pure*	*4.5 h*	*12 h*	*24 h*	*72 h*	*NMC 811*	*pure*	*4.5 h*	*12 h*	*24 h*	*72 h*
X-Ray: Cu	+	+	+	+	+		+	+	+	+	+		+	+	+	+	+
HRFD	+	+	+	+	+		+	+	+	+	+		+	+	+	+	+

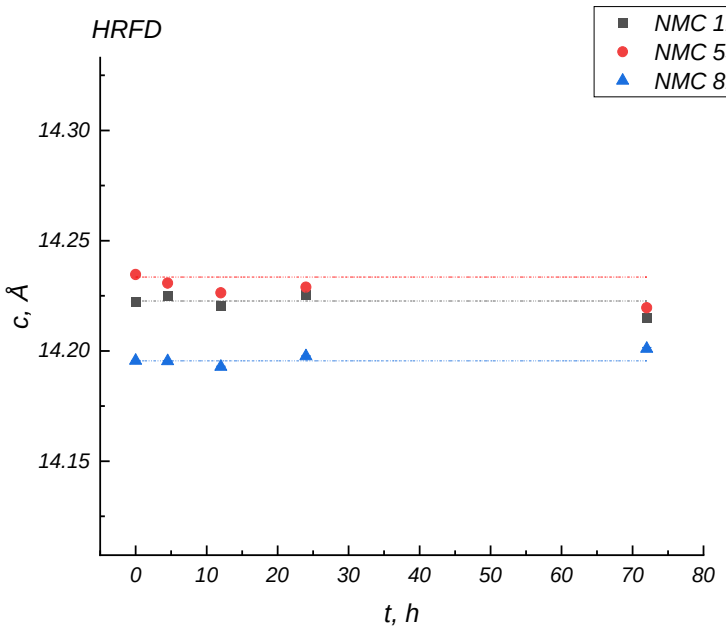
Structural study. Neutron Diffraction data and results of Rietveld method data processing.

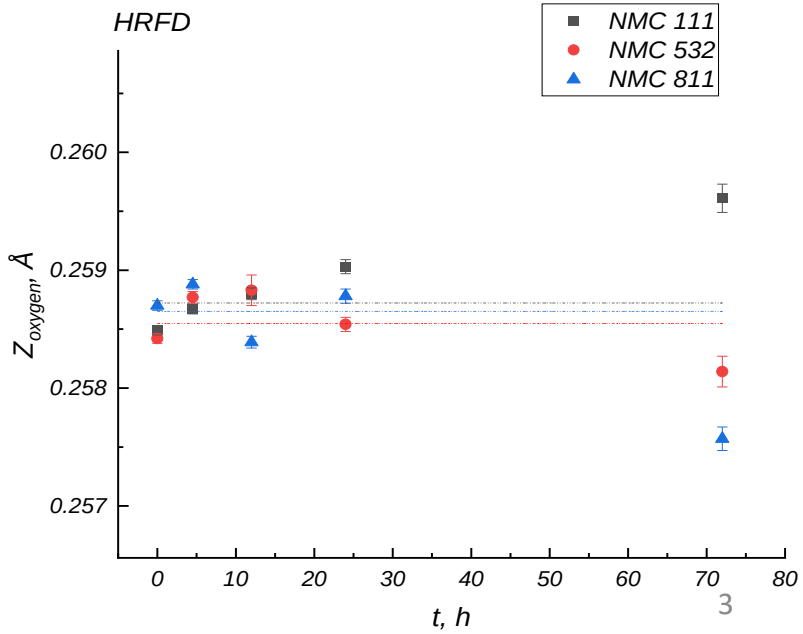








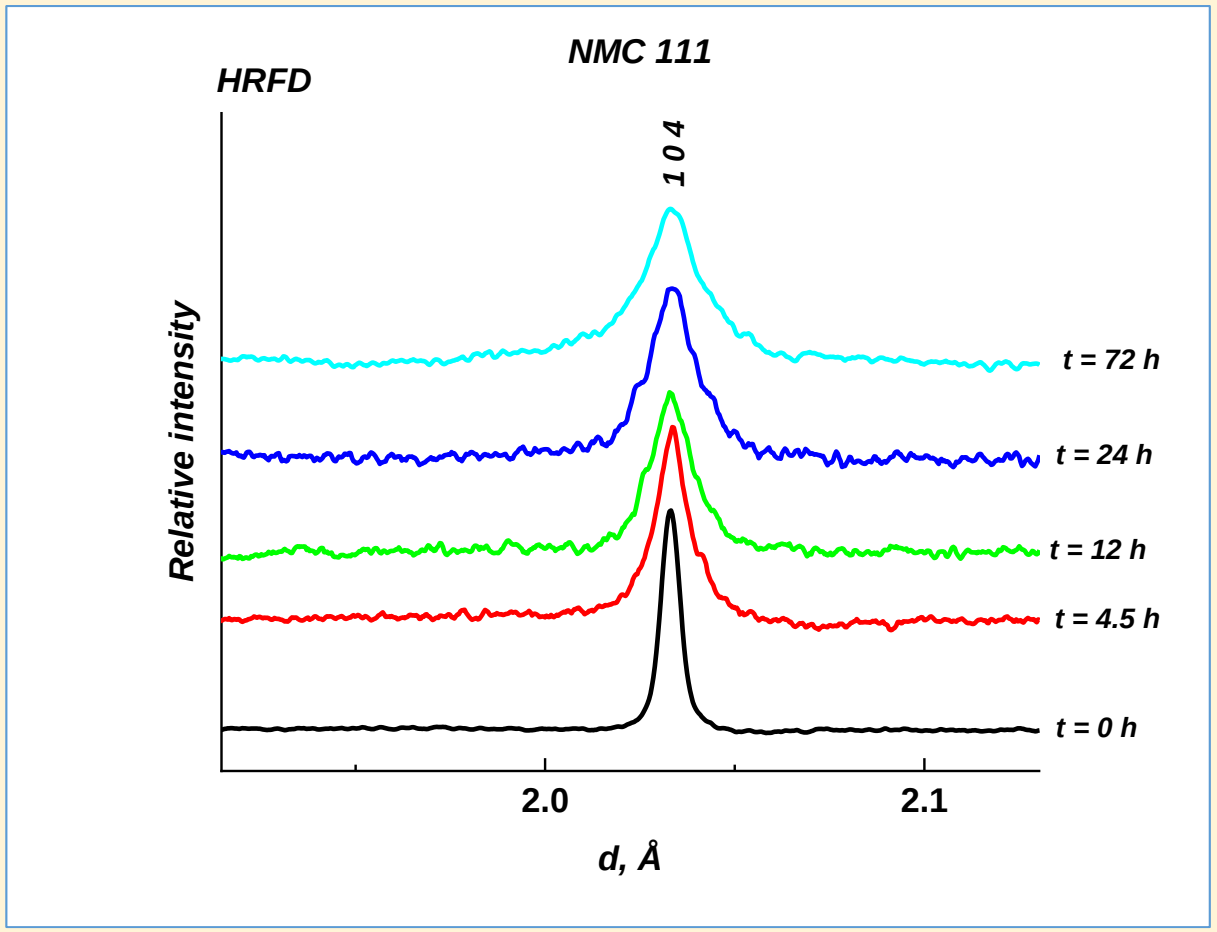


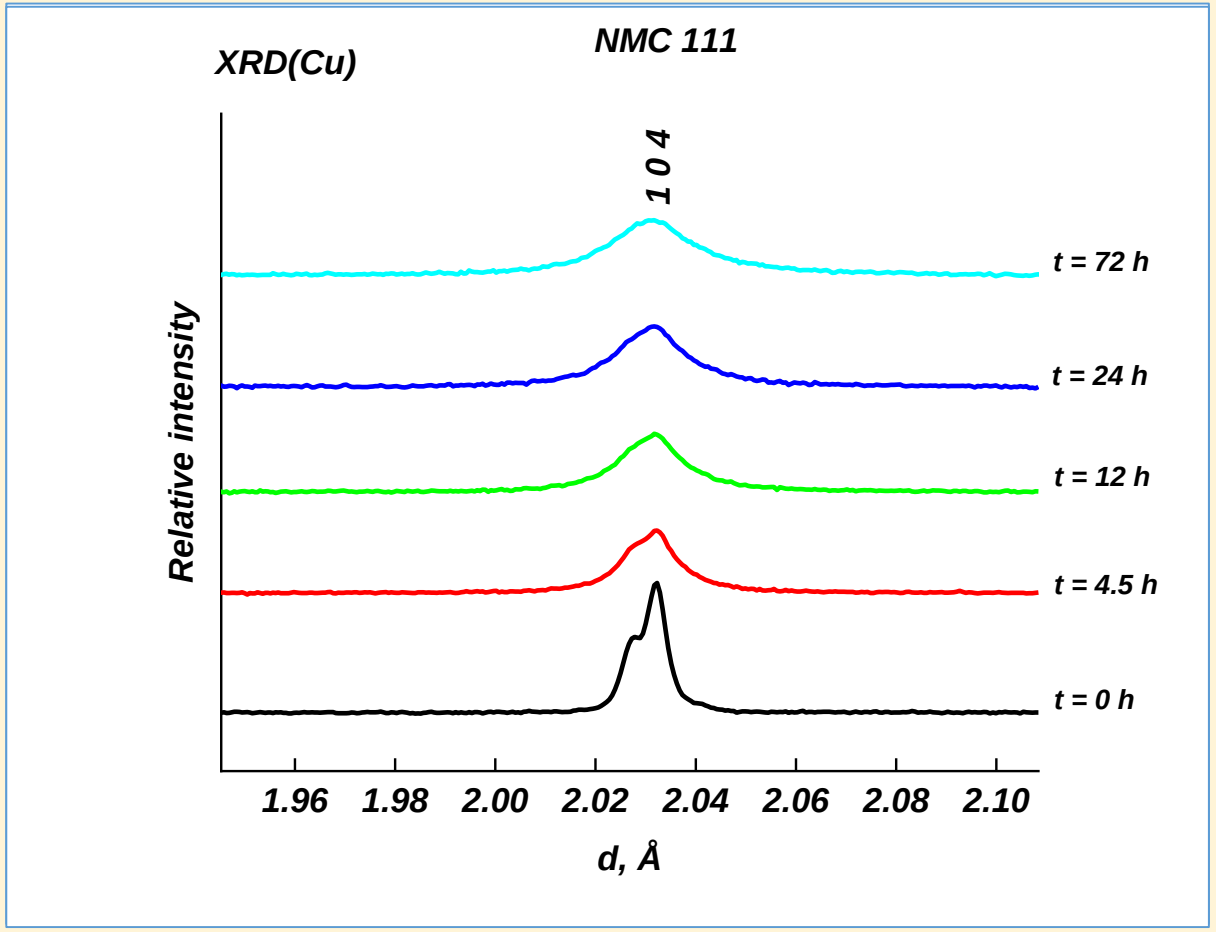


Structural study.

Diffraction patterns analysis.

Diffraction spectra from as-received and ball milled NMC 111 samples: t = 0, 4.5, 12, 24, 72 h





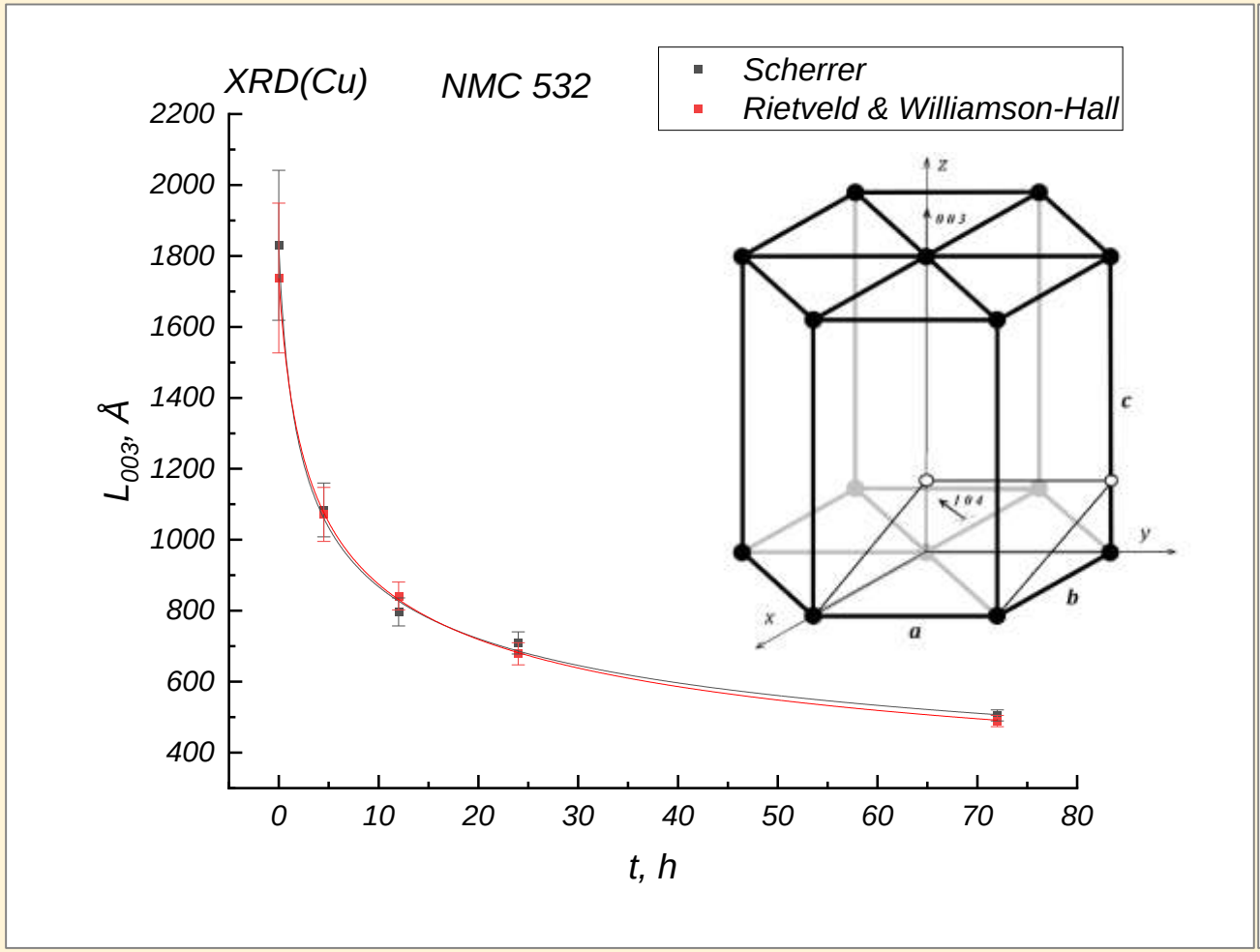
Peak widths' broadening ⇒ microstructural changes

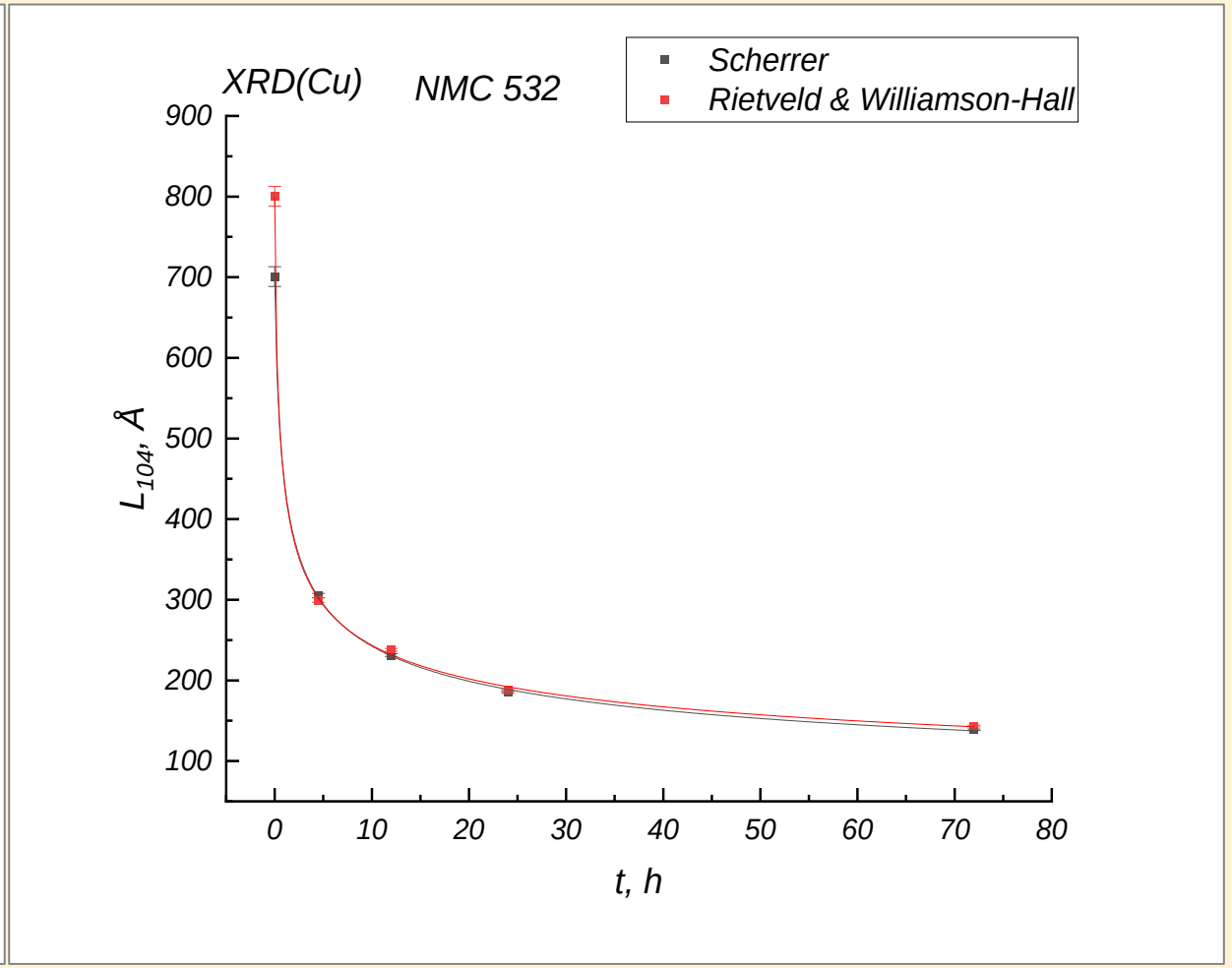
Structural study.

Diffraction patterns processing.

Rietveld method with Williamson-Hall formula (1) embedded in it.

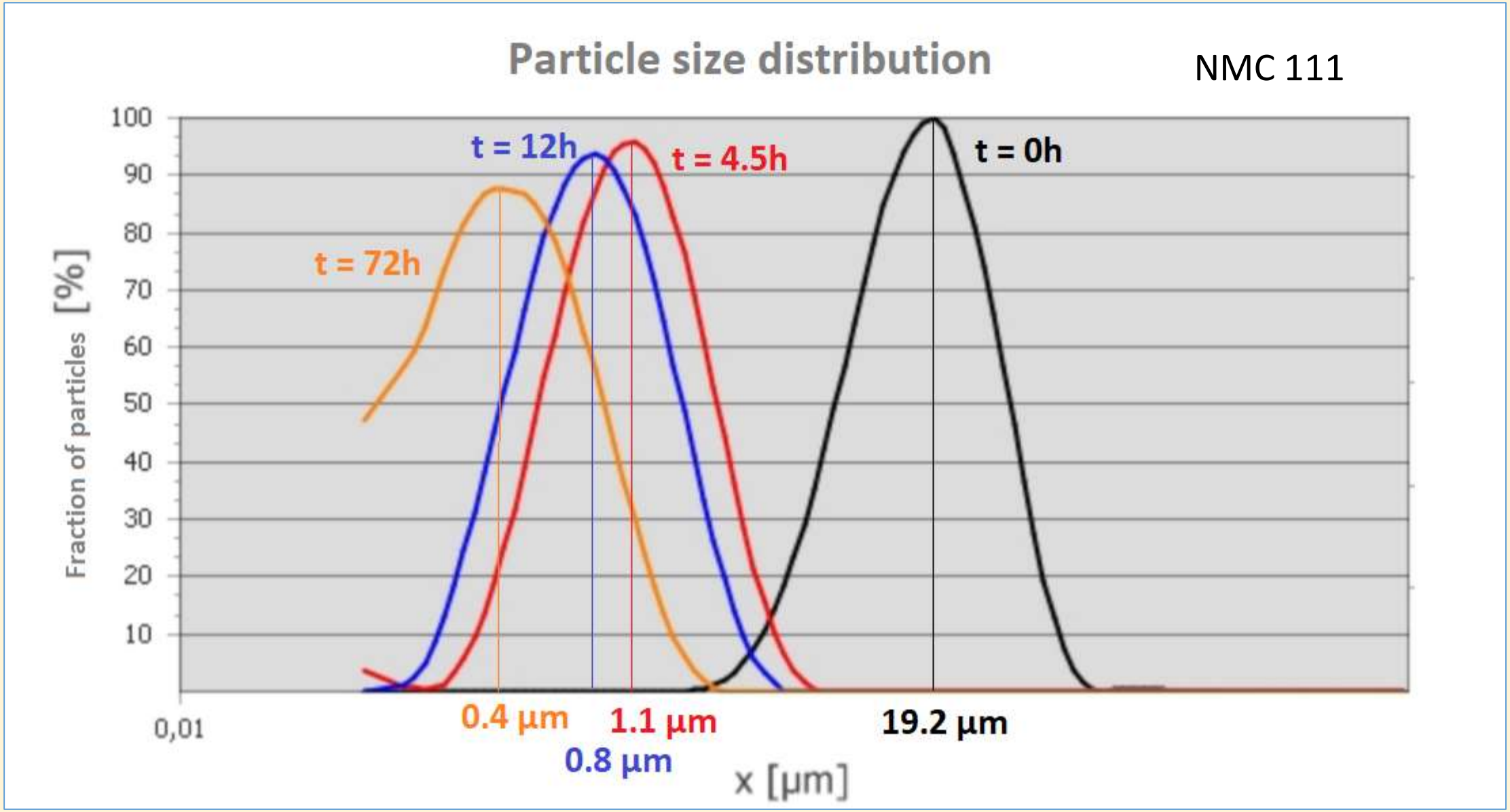
$$\beta(2\theta) = \beta_{instr} + \frac{K\lambda}{Lcos(\theta)} + 2\varepsilon\, tg(\theta) \quad (1)$$





This processing method was implemented in the FullProf program.
It showed good agreement with the data obtained by the Scherrer method.

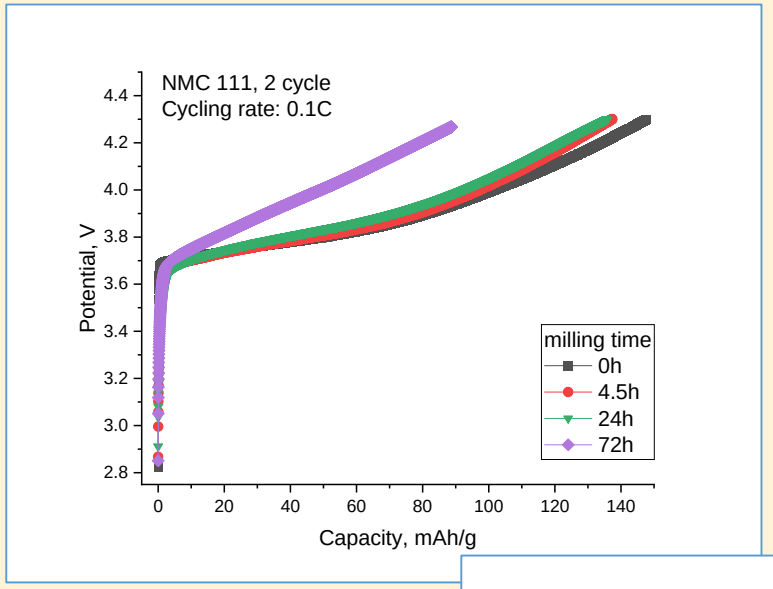
Structural study. Laser diffraction data. Particle size distribution.

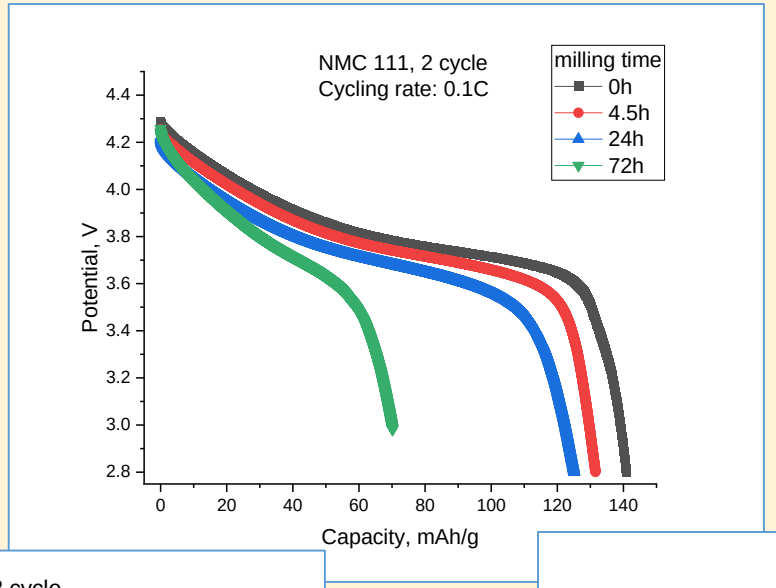


Electrochemical study

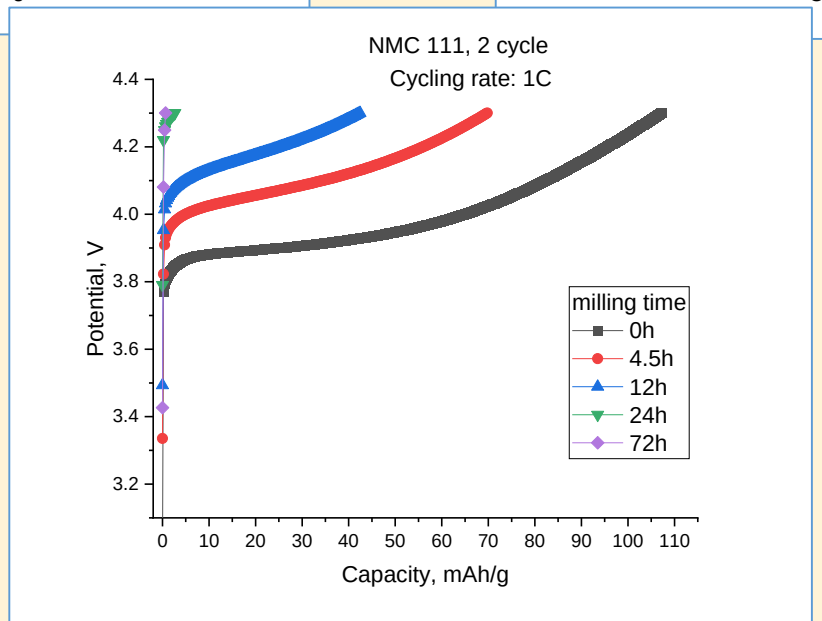
$$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 \leftrightarrow Li_{(1-x)}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 + xLi^+ + xe^-$$

Charging/discharging curves for NMC 111 samples. Cycling rates: 0.1C, 1C.

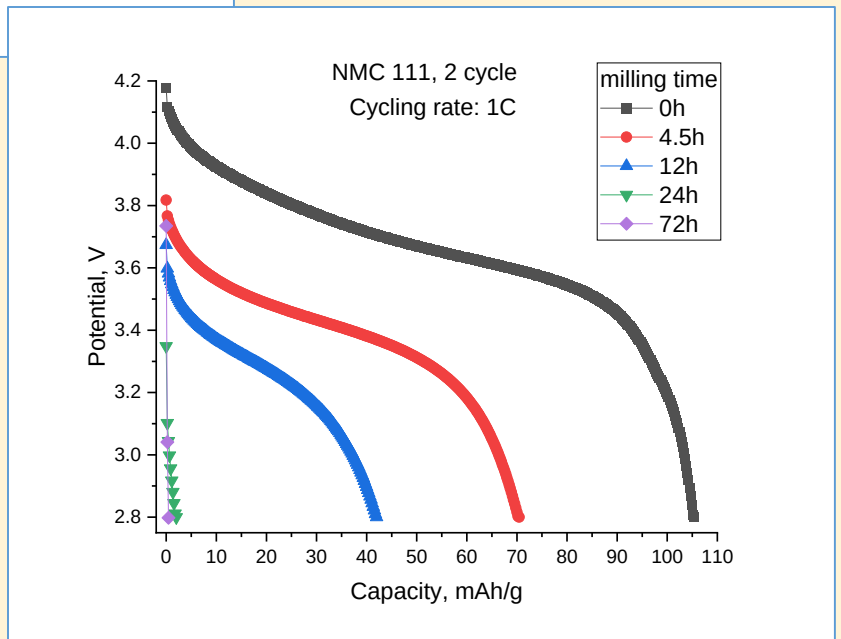




Capacity reduction is observed for all ball milled samples in comparison to as-received material.



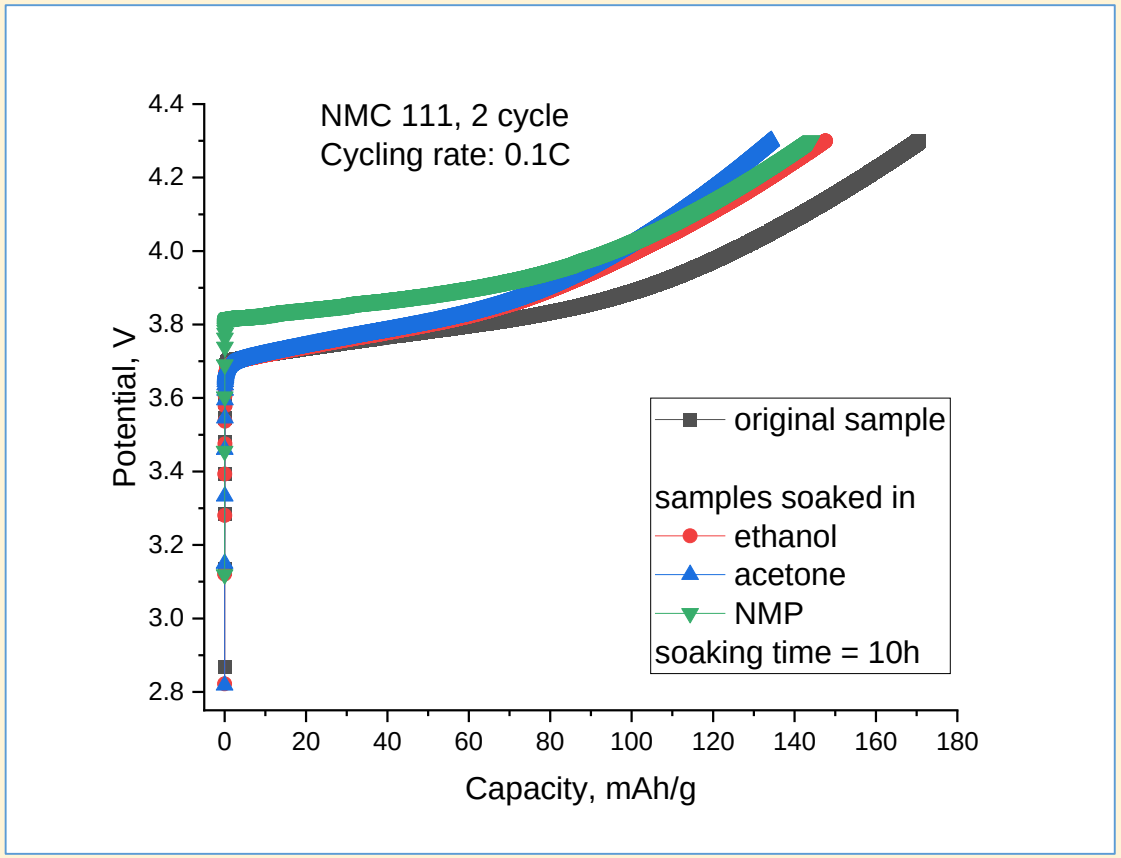
Electrochemical performance parameters are decreasing as the milling time increases.

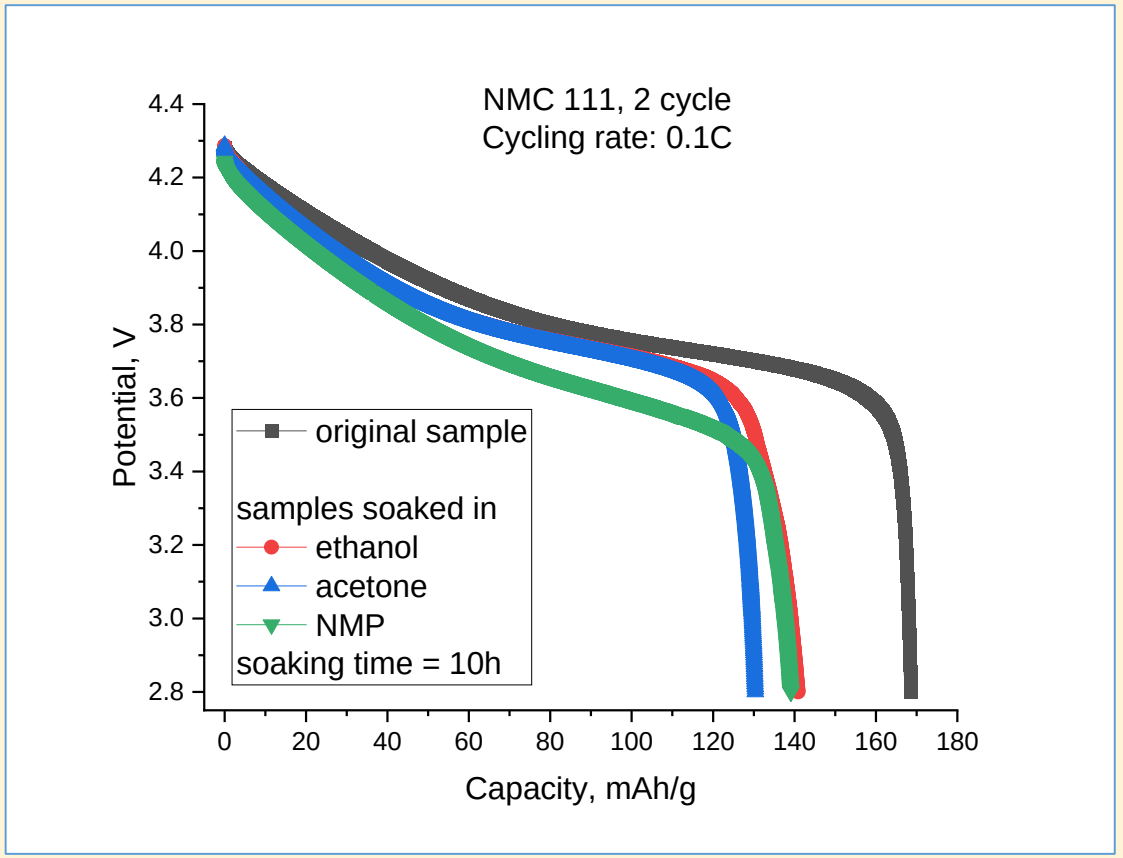


Electrochemical study

$$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 \leftrightarrow Li_{(1-x)}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 + xLi^+ + xe^-$$

Charging/discharging curves for not milled NMC 111 soaked in different solvents. Cycling rate: 0.1C.





Solvents seem to have an impact on cell performance => liquid for milling should be chosen carefully.

Results

Structural study

→ milling does not significantly affect the crystal structure of the studied cathode materials.

- Crystallite size correlates directly to milling time.
- The longer the milling time period, the lower the effectiveness of crystallite size-reduction.
- Coherently scattering regions have anisotropic sizes induced by hexagonal crystal symmetry of NMC.

Electrochemical study (preliminary results)

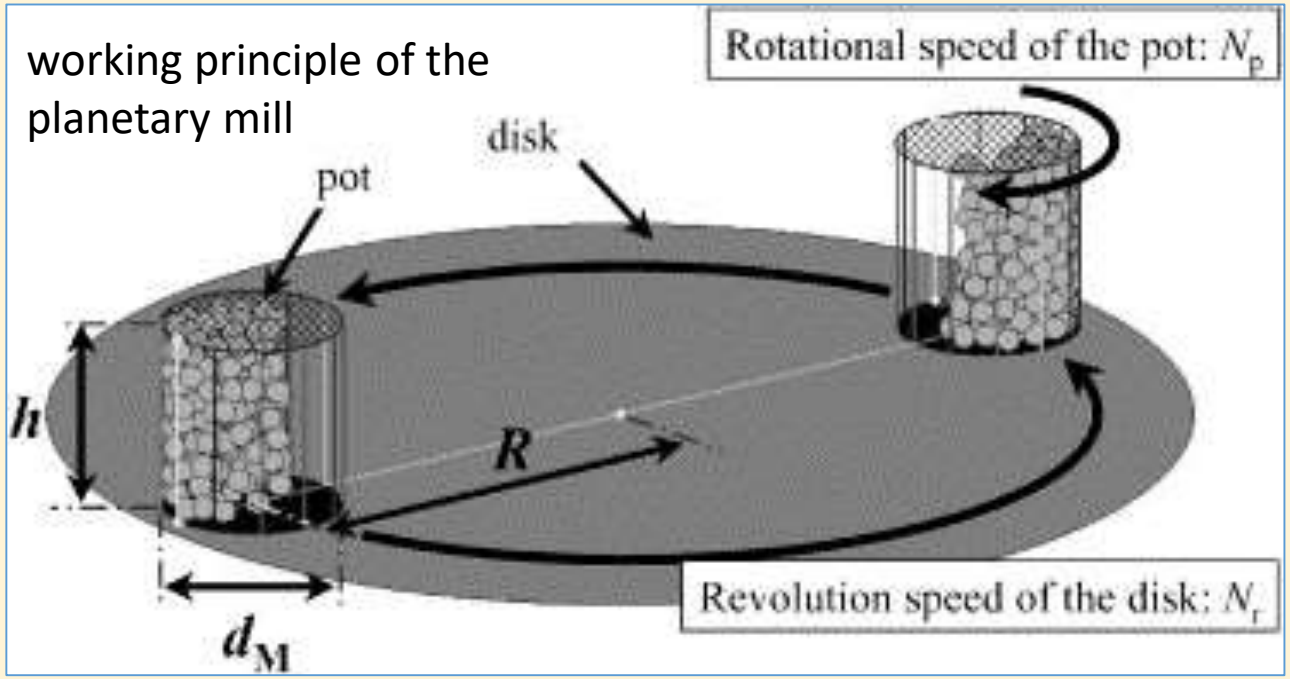
→ ball milling leads to capacity loss and deterioration of high-rate charge/discharge characteristics.

- Solvents in which milling is carried out have an impact on cell performance.

Thank you for your attention!

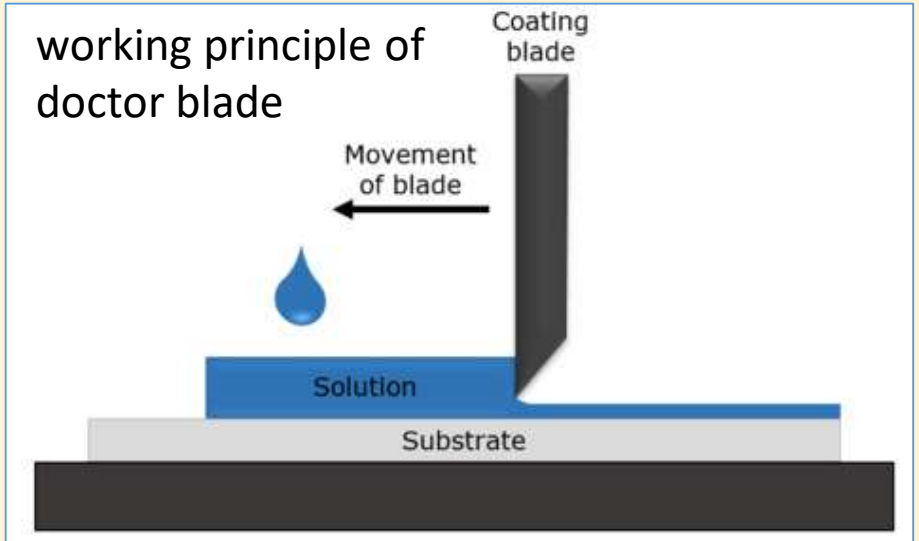
Experimental part

working principle of the planetary mill

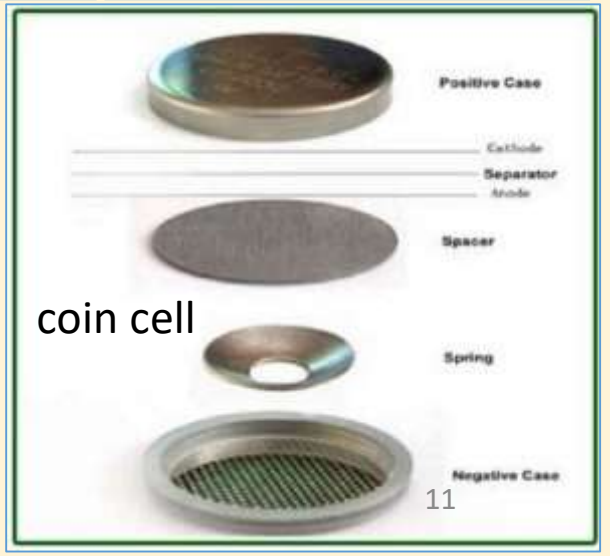


Planetary ball mill

working principle of doctor blade



doctor blade

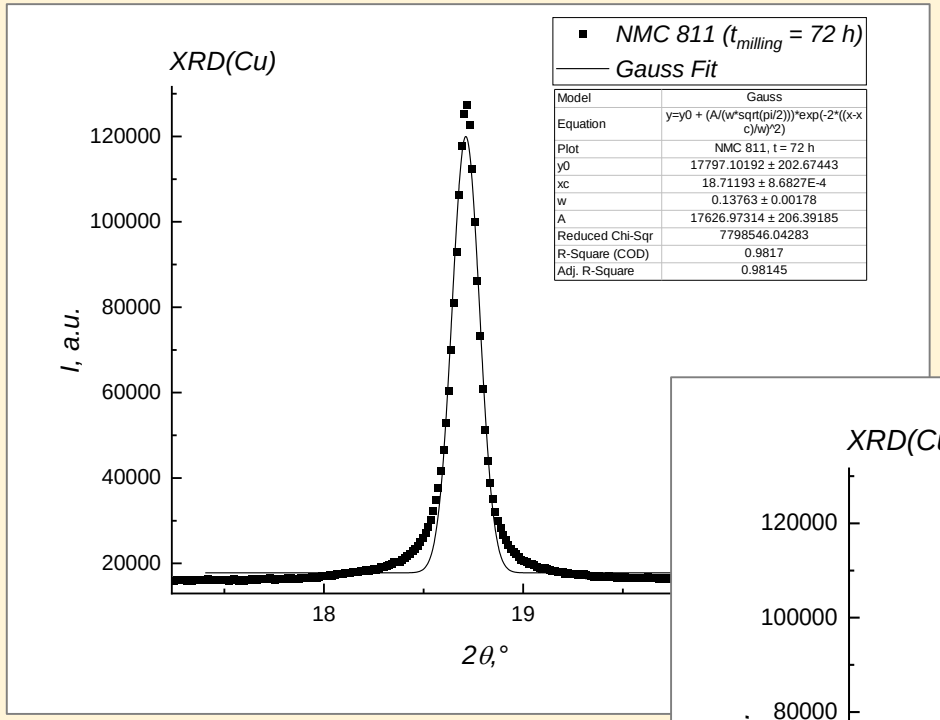


coin cell

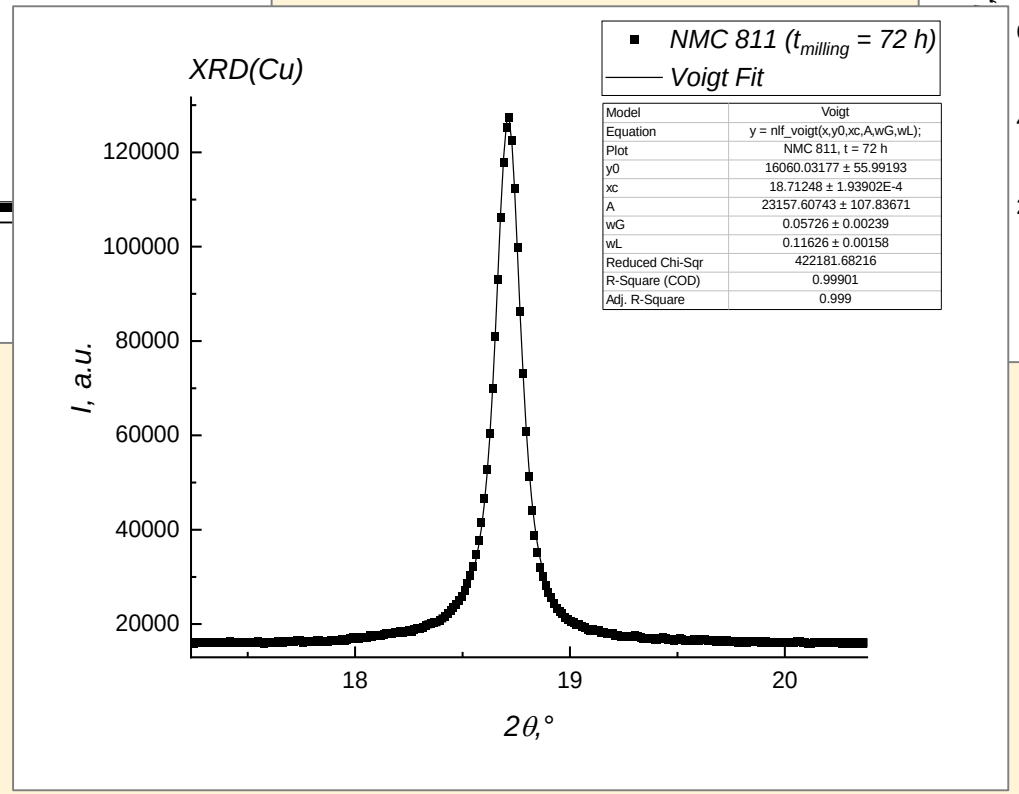
Structural study.

Diffraction patterns analysis.

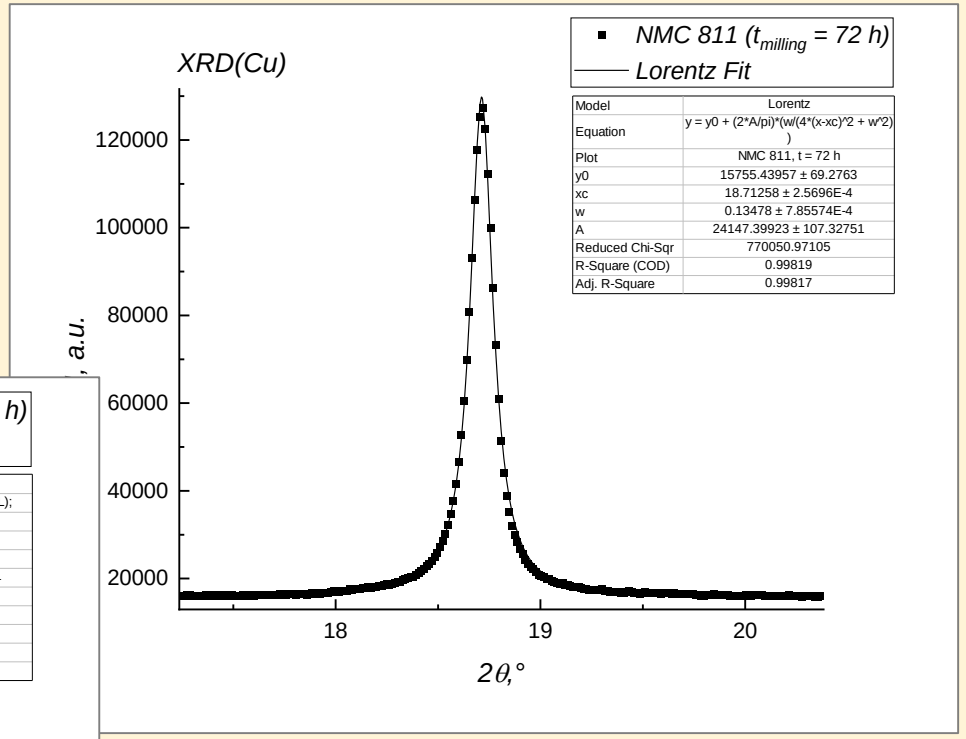
Individual peak's approximation via Gauss, Lorentz and Voight functions.



Model	Gauss
Equation	y=y0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)
Plot	NMC 811, t = 72 h
y0	17797.10192 ± 202.67443
xc	18.71193 ± 8.6827E-4
w	0.13763 ± 0.00178
A	17626.97314 ± 206.39185
Reduced Chi-Sqr	7798546.04283
R-Square (COD)	0.9817
Adj. R-Square	0.98145



Model	Voigt
Equation	y = nlf_voigt(x,y0,xc,A,wG,wL);
Plot	NMC 811, t = 72 h
y0	16060.03177 ± 55.99193
xc	18.71248 ± 1.93902E-4
A	23157.60743 ± 107.83671
wG	0.05726 ± 0.00239
wL	0.11626 ± 0.00158
Reduced Chi-Sqr	422181.68216
R-Square (COD)	0.99901
Adj. R-Square	0.999

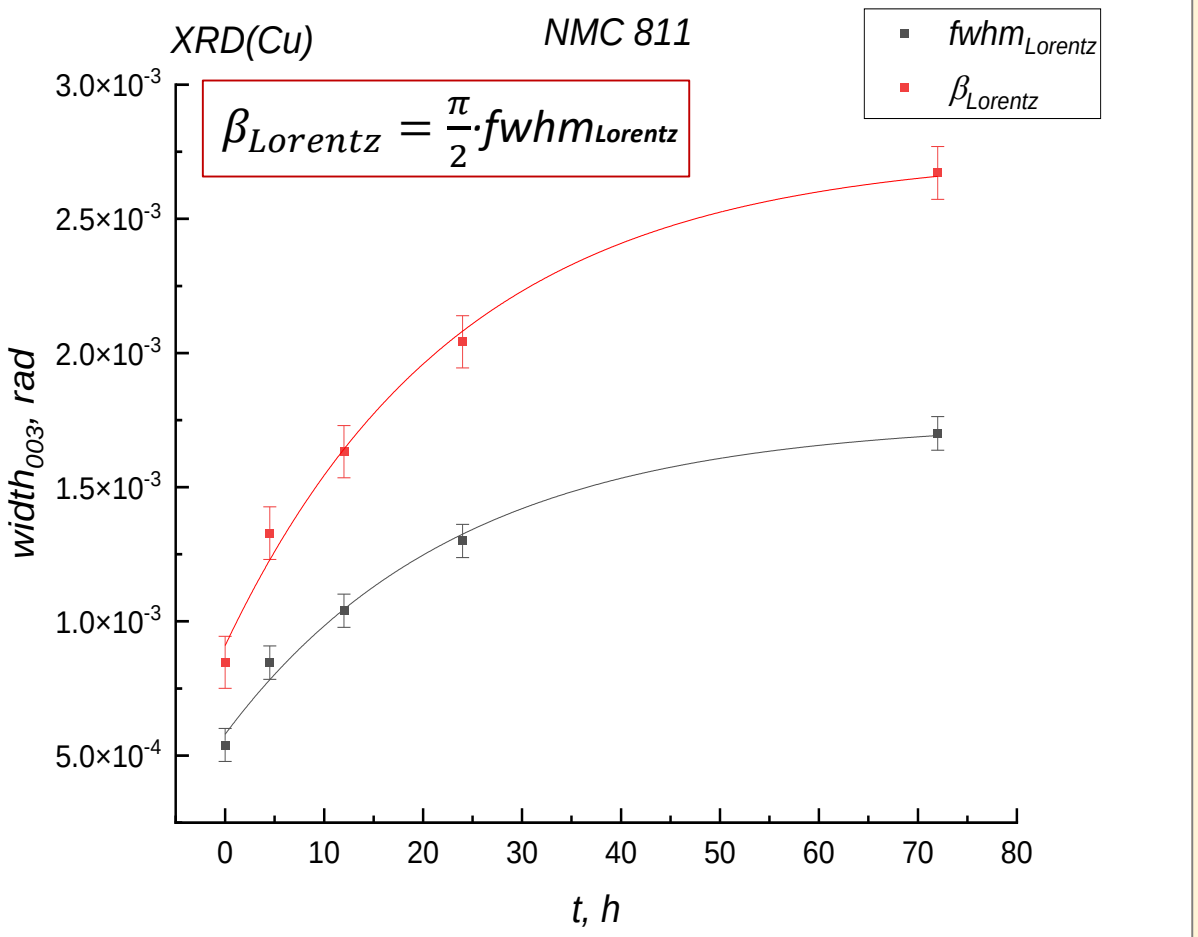


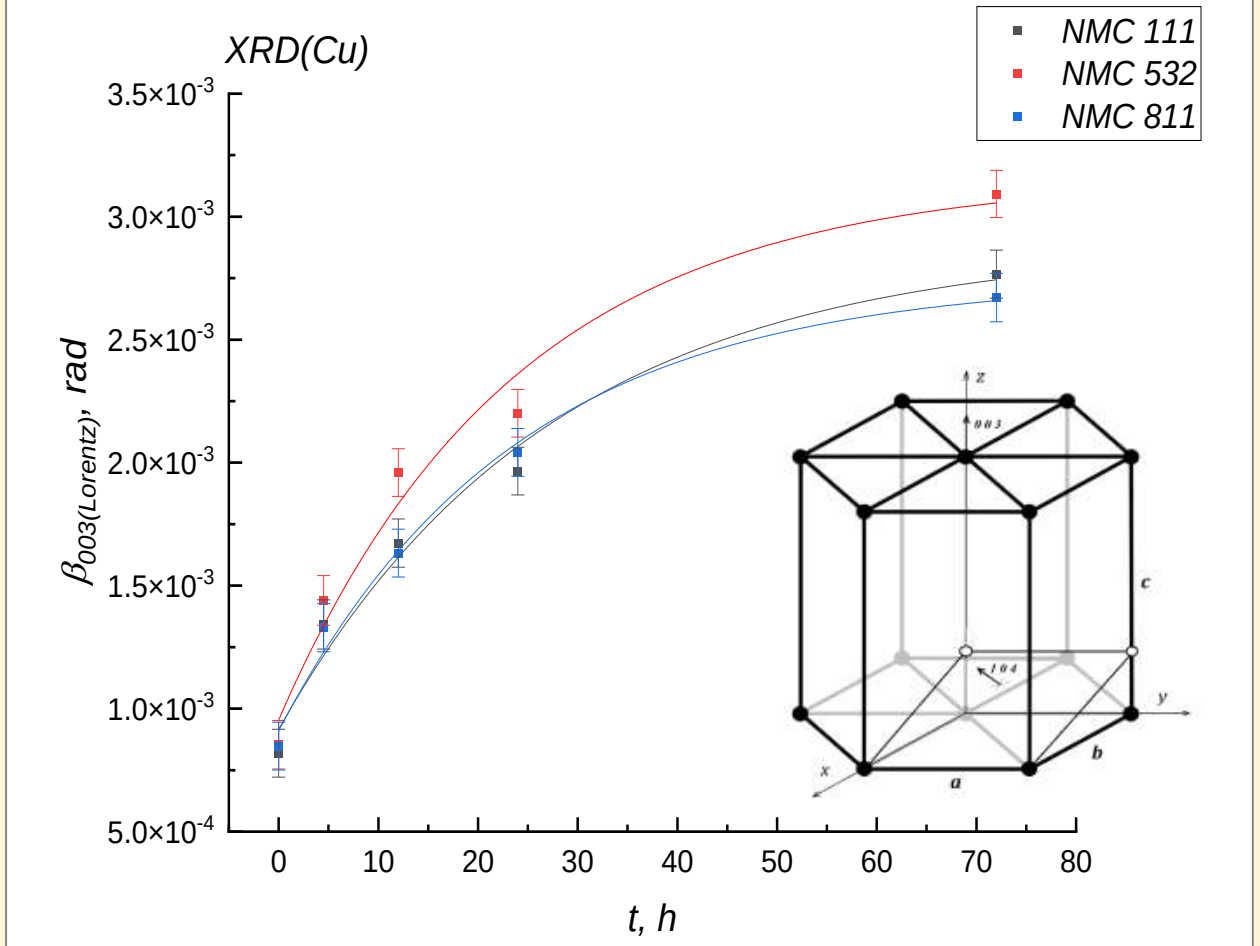
Model	Lorentz
Equation	y = y0 + (2*A/pi)*(w/(4*(x-xc)^2 + w^2))
Plot	NMC 811, t = 72 h
y0	15755.43957 ± 69.2763
xc	18.71258 ± 2.5696E-4
w	0.13478 ± 7.85574E-4
A	24147.39923 ± 107.32751
Reduced Chi-Sqr	770050.97105
R-Square (COD)	0.99819
Adj. R-Square	0.99817

Structural study.

Diffraction patterns analysis.

Integral width of the 003 reflex dependence on milling time.



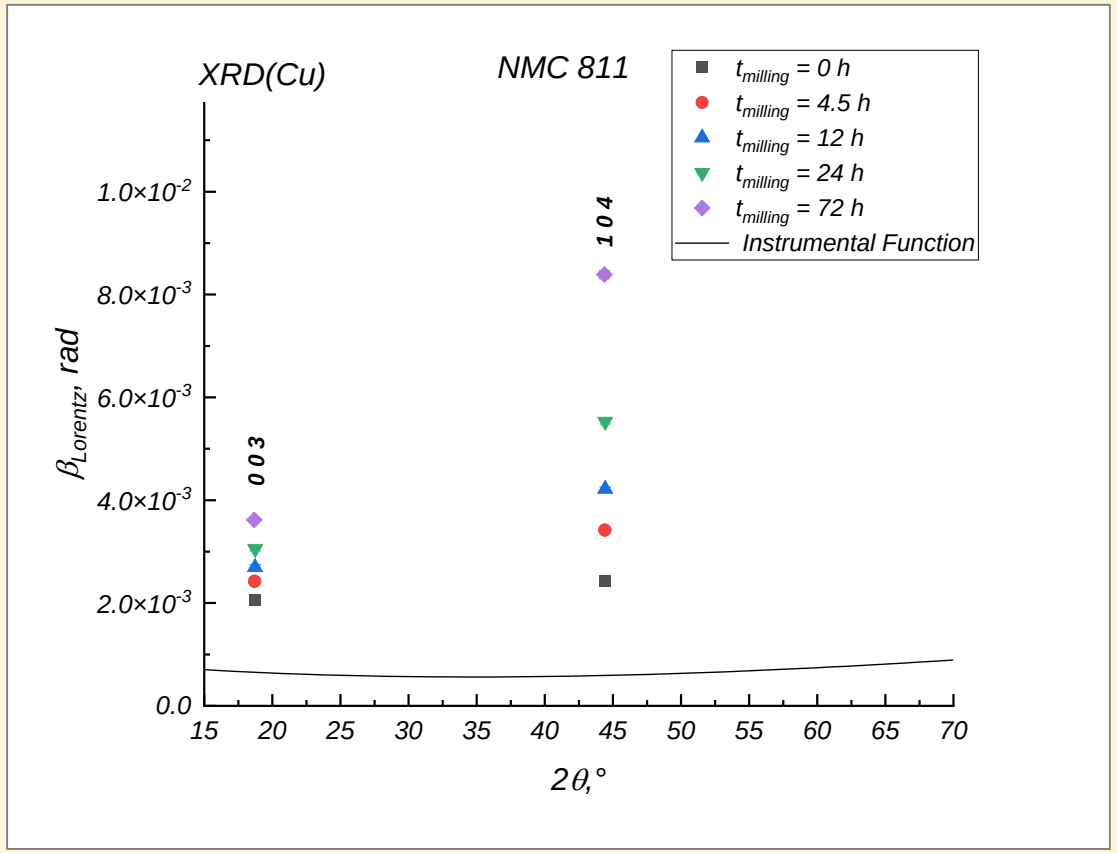


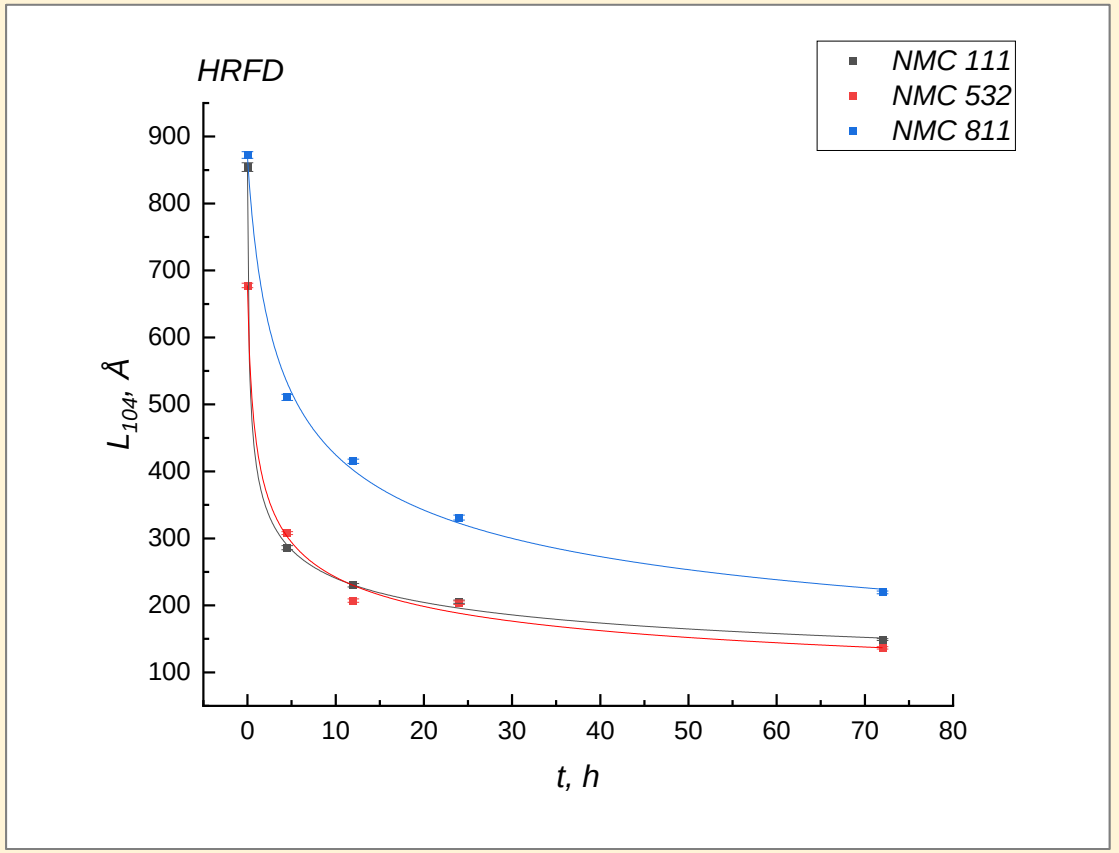
Structural study.

Diffraction patterns processing.

Scherrer method. Stokes' correction.

$$\beta(2\theta) = \beta_{instr} + \beta_S = \beta_{instr} + \frac{K\lambda}{Lcos(\theta)}$$





NMC 811	t, h		0	4.5	12	24	72
	L, Å	XRD	834 ± 18	564 ± 8	446 ± 6	329 ± 4	210 ± 2
		HRFD	872 ± 5	511 ± 5	415 ± 3	331 ± 4	220 ± 2

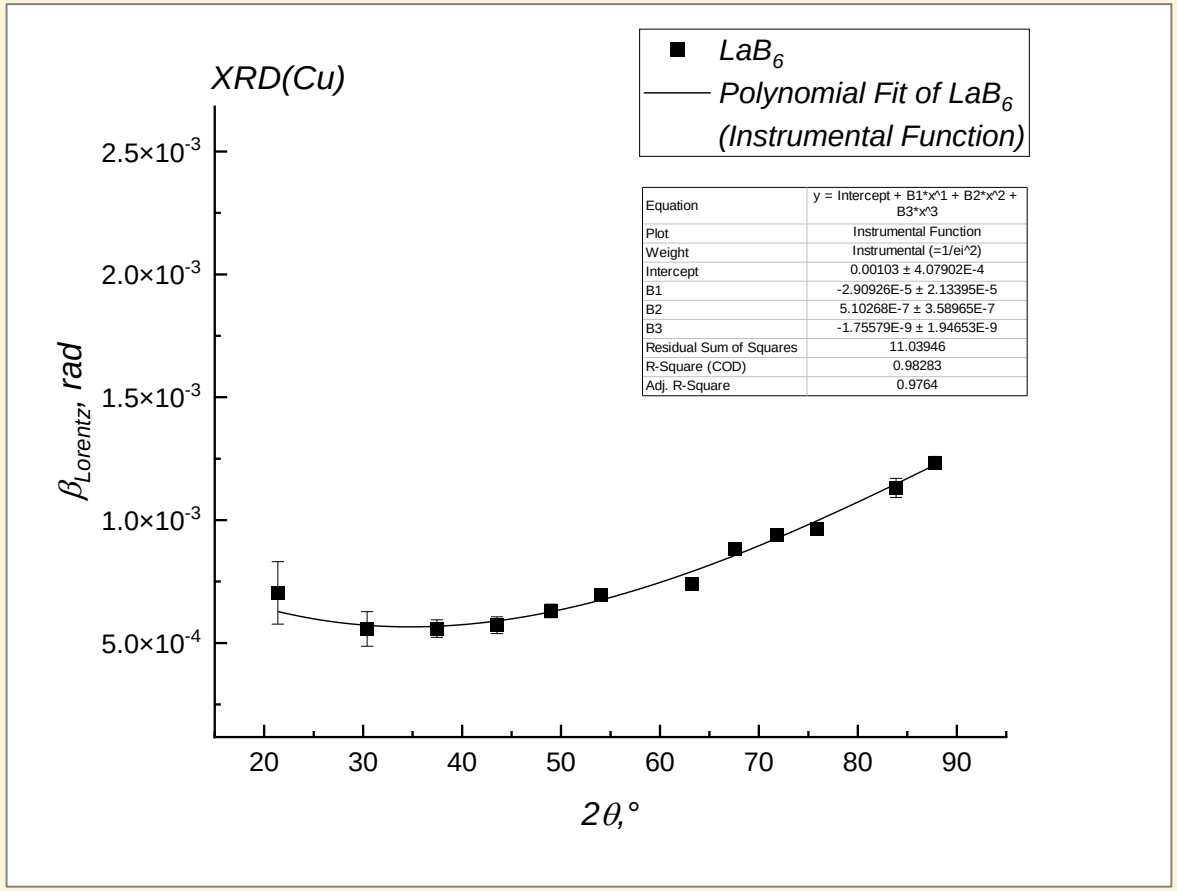
Structural study.

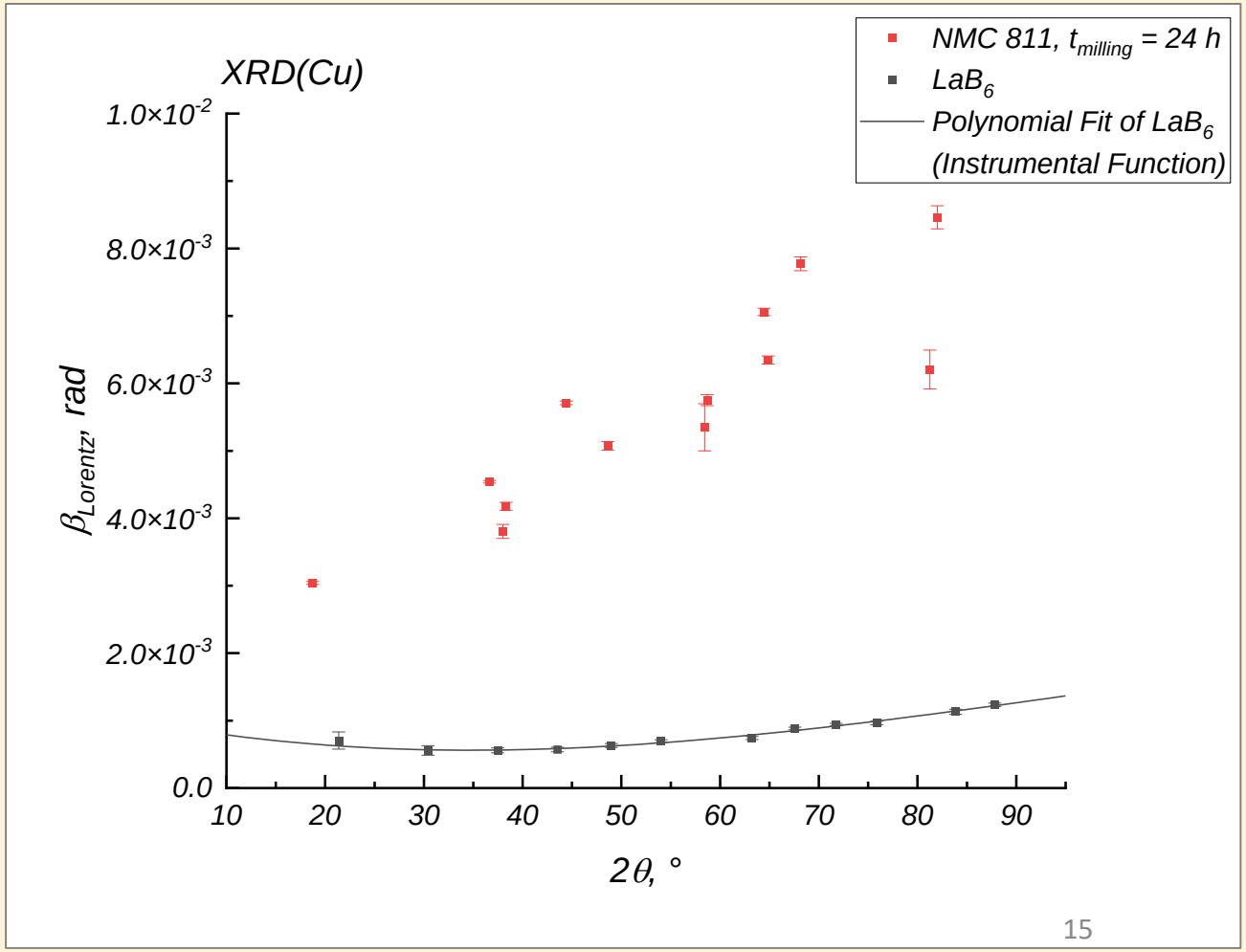
Diffraction patterns procesing.

Williamson-Hall method.

$$\beta_S(2\theta) = \frac{K\lambda}{L\cos(\theta)} \qquad \beta_D = 2\,\varepsilon\, tg(\theta)$$

$$\beta(2\theta) = \beta_{instr} + \frac{K\lambda}{L\cos(\theta)} + 2\varepsilon\, tg(\theta).$$



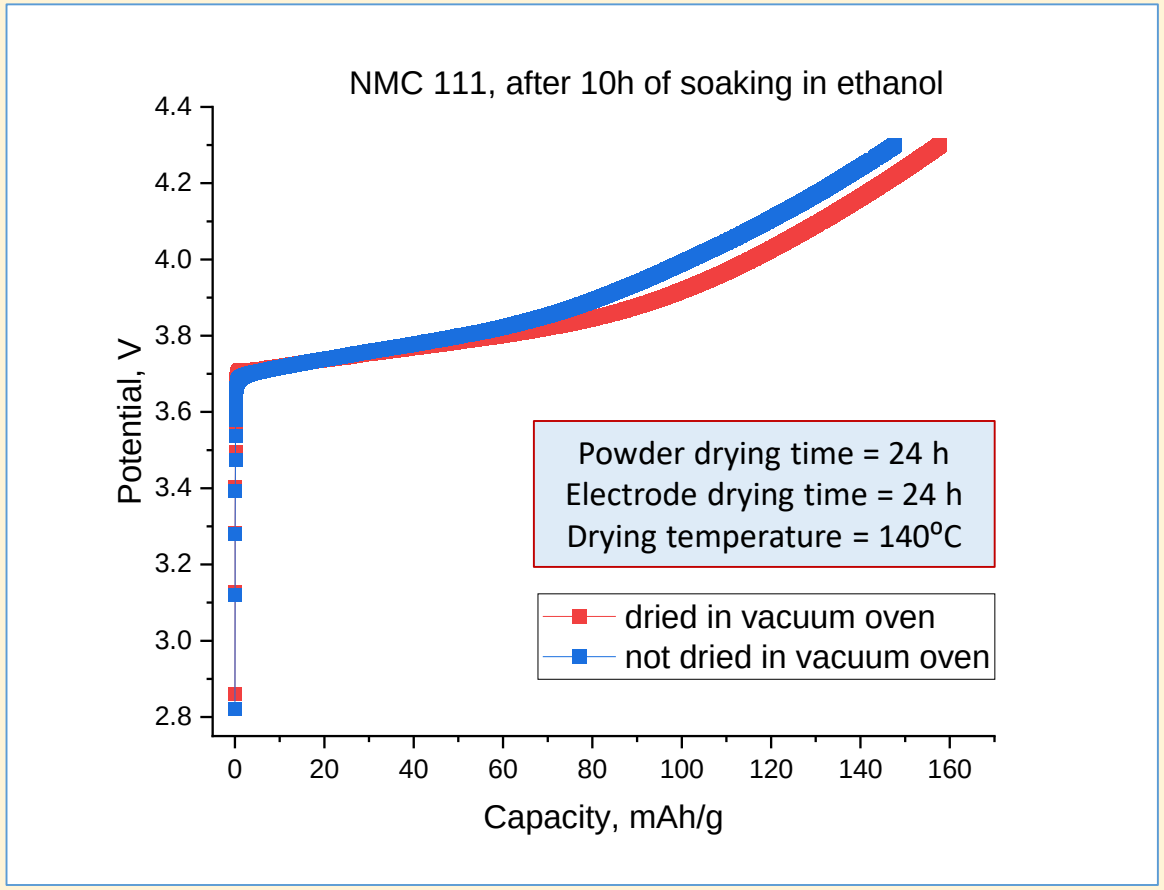


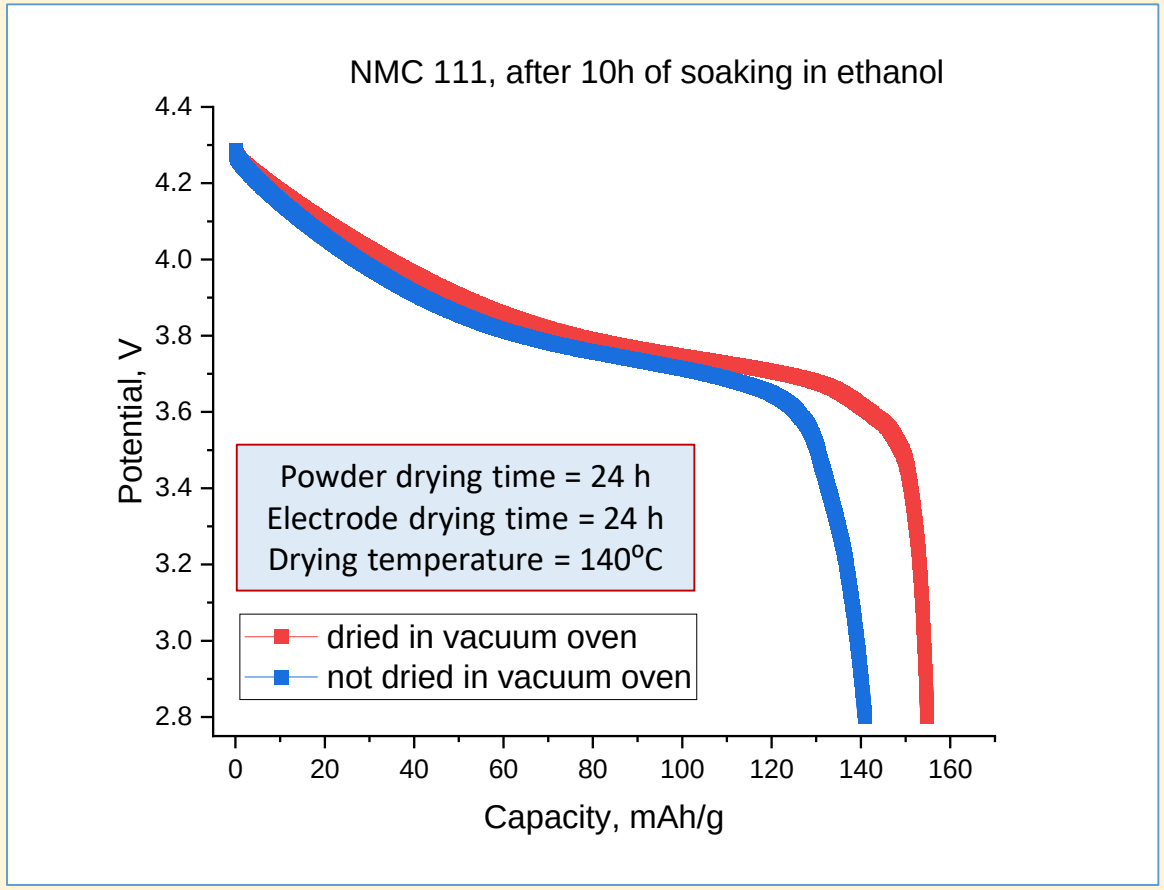
Strong diffraction peak widths ***anisotropy*** is observed. This fact significantly complicates further processing by the Williamson-Hall method.

Electrochemical study

$$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 \leftrightarrow Li_{(1-x)}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2 + xLi^+ + xe^-$$

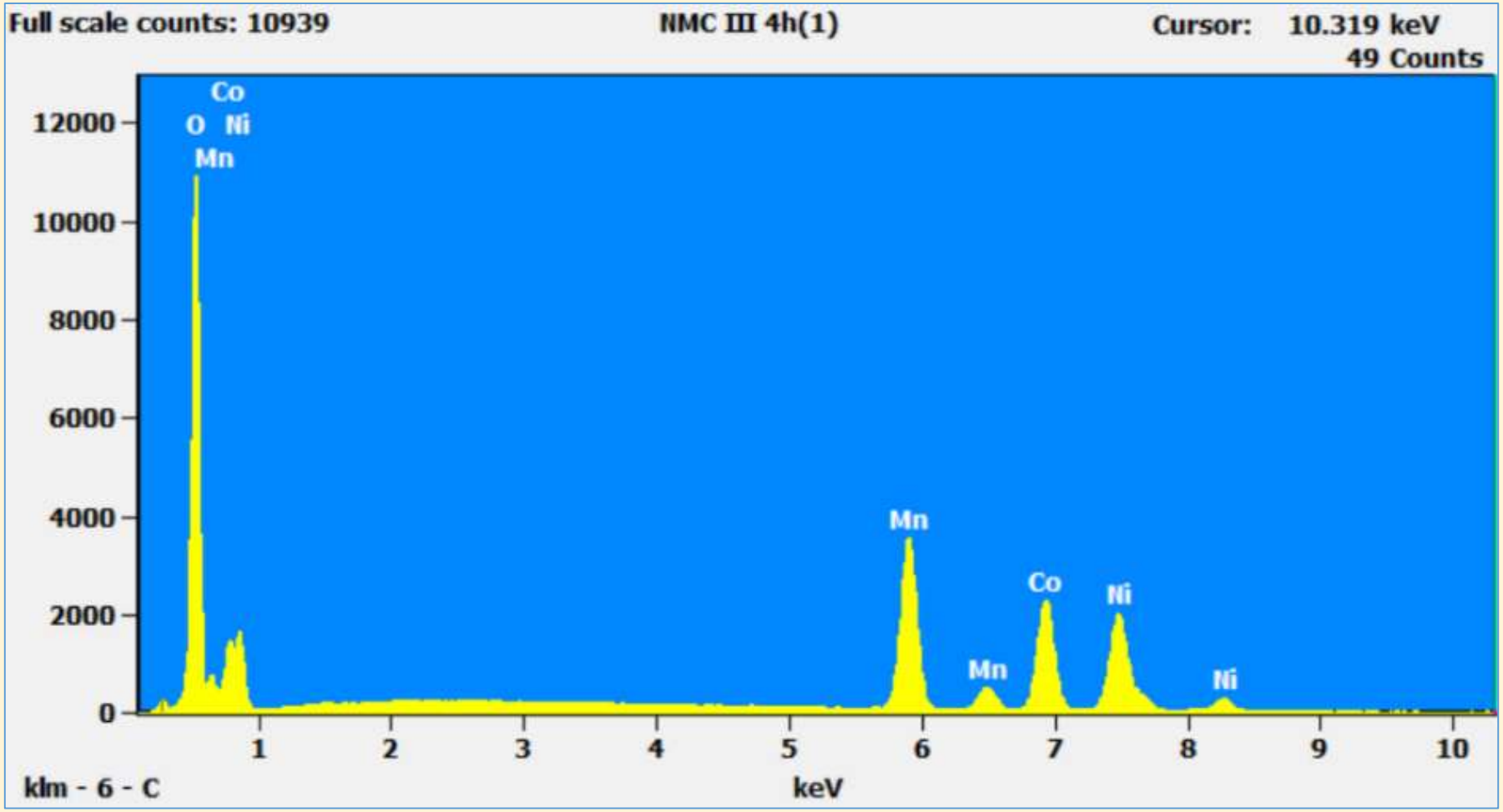
Charging/discharging curves for NMC 111 soaked in ethanol for 10 h and was/wasn't dried in vacuum oven. Cycling rate: 0.1C.





Empirically obtained: drying conditions do affect electrochemical performance characteristics!

Structural study. Energy Dispersive X-Ray Analysis.



Element Line	Weight %	Weight % Error	Norm. Wt.%	Atom %	Atom % Error
O K	31.67	± 0.17	31.67	62.47	± 0.34
Mn K	22.96	± 0.12	22.96	13.19	± 0.07
Co K	22.62	± 0.13	22.62	12.11	± 0.07
Ni K	22.75	± 0.14	22.75	12.23	± 0.08
Total	100.00		100.00	100.00	