#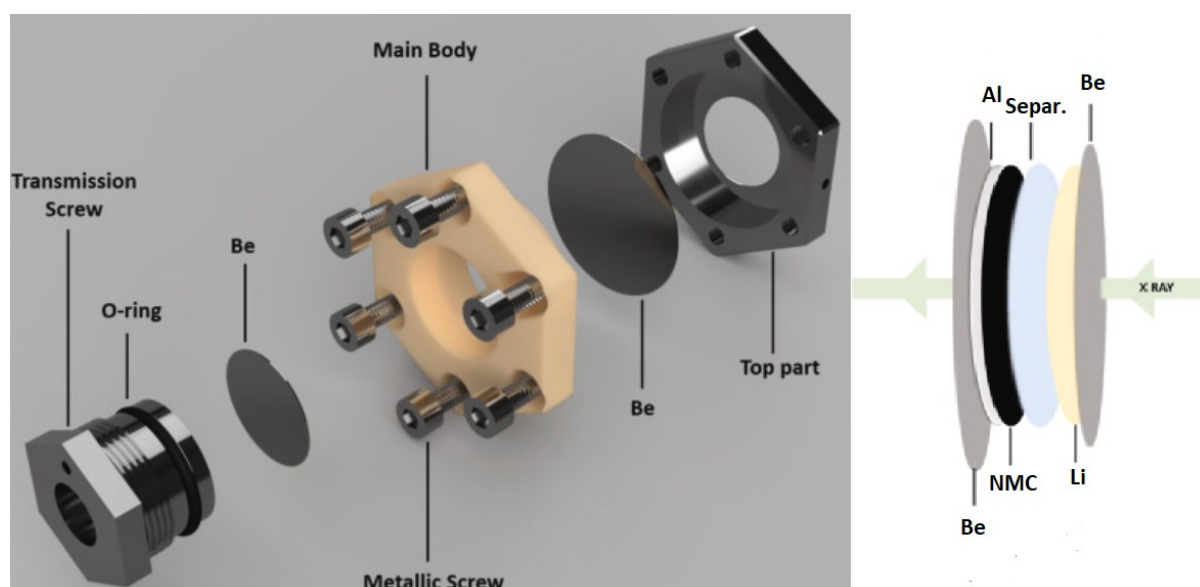 Sequential refinement by the Rietveld Method of an *operando* electrochemical cell with solid solution $LiNi_{0.333}Mn_{0.333}Co_{0.333}O_2$ battery material with FullProfAPP.

In this exercise we will show an *operando* X-ray diffraction measurement of an electrochemical cell that contains $LiNi_{0.333}Mn_{0.333}Co_{0.333}O_2$ (NMC111) as the active material. The experiment was carried out at the NOTOS beamline at ALBA synchrotron ($\lambda = 1.12698$ Å) in the $8.7^\circ - 51.6^\circ$ 2θ range. Different from yesterday's example ($LiFePO_4$), a **hexagonal LeRiChe v2.0** electrochemical cell was used.

Below you can find the scheme of the operando electrochemical cell used for this example. The experiment is carried out in transmission mode. The cell stack (right picture) is now sandwiched between two Beryllium windows.
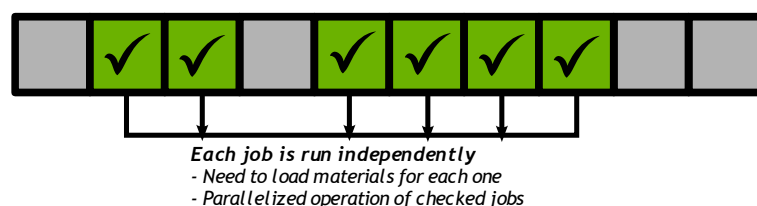

Examples/NMC111/1-s2.0-S0378775322012472-main.pdf

Upon normal electrochemical operations NMC111 is known to have a solid solution. This means that upon oxidation and reduction, intermediate Li compositions are thermodynamically stable against phase separation. This, of course, constitutes a simplified vision of what really happens in this class of complex materials. Indeed, depending on the operating conditions and composition, these materials can undergo phase transformations into isostructural H1, H2, and H3 phases, or even transform into O1, rock-salt, and spinel phases. However, for the purpose of simplifying the analysis, we can assume that the NMC111 is evolving with a solid solution mechanism.

In the experimental data provided in **'Examples/NMC111/IS22NMCapd'** we omitted the patterns that correspond to the first charge/discharge cycle (formation cycle) of the electrochemical cell, where some of the abovementioned phases can be observed. Instead, you should only expect a set of smoothly varying diffraction peaks along the pattern series, without shoulders and peaks that could suggest the appearance of new phases. An instrumental resolution function is also provided in **'Examples/NMC111/IRF_NOTOS_July2022_MR.irf'**.
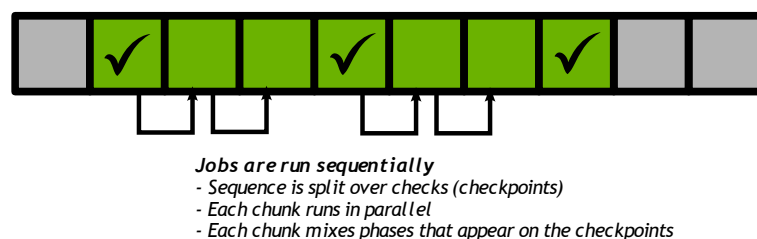
Exercise:

1. Select the **'Examples/NMC111/'** as the working directory.
2. Load the experimental data onto the app.
3. Explore your data using the arrows buttons and the 'Contour Plot' button.
4. **Check** the appropriate patterns for the analysis using the 'Pattern Checks' option. Just as we mentioned yesterday, the objective of this exercise is to perform a sequential refinement. Pay special attention to how the *'Automatic Refinement Protocol'* window changes the app's behavior when the *'Sequential Mode'* box is checked. (Read more information in the web manual).

Normal Mode

Each job is run independently
- Need to load materials for each one
- Parallelized operation of checked jobs

Sequential Mode

Jobs are run sequentially
- Sequence is split over checks (checkpoints)
- Each chunk runs in parallel
- Each chunk mixes phases that appear on the checkpoints

5. Use the app to extract the **background** points.
6. **Download CIF** files from the Crystallographic Open Database using the app's client. Remember that, apart from the **Aluminum** foil (current collector), the *operando* cell contains two **Beryllium** windows.
7. Use the 'Simulate Selection' option to find the CIF files that have initial parameters that are good enough to be used as a **first guess** for the refinement process. Use the 'Generate CIF' option in the simulation window if necessary to create new CIF files with better cell parameters.
8. Load the correct CIF files on the *'Automatic Refinement Protocol'* window.
9. Select the appropriate refinement strategy and parameters.
10. The signals that correspond to the Beryllium windows do not overlap with the NMC111 peaks and we can just exclude them from the refinement.
11. Perform the **sequential refinement**. Does the evolution of the **a** and **c** cell parameters correspond to the behavior found in literature? Is the refinement satisfactory?

Extra Exercises:

1. Include the Beryllium window signals into the refinement. As you can see from the scheme of the hexagonal LeRiChe v2.0 cell, the diffraction planes of both windows are separated from one another. This means that you will have to include two different sets phase dependent shifts for each window. You can do this with the *'Manual Refinement´* window.

2. Load the correct CIF files (including two beryllium phases) into the *'Manual Refinement'* window.
3. Check the 'MORE' tag of all phases.
4. Check the 'Ph_Shift' tag on all phases.
5. Manually vary the phase dependent shifts and find a good initial guess for the refinements.
6. Load the newly generated PCR file into the *'Automatic Refinement Protocol'* window and perform another **sequential** refinement, but this time including the phase dependent shifts in the refinement strategy.