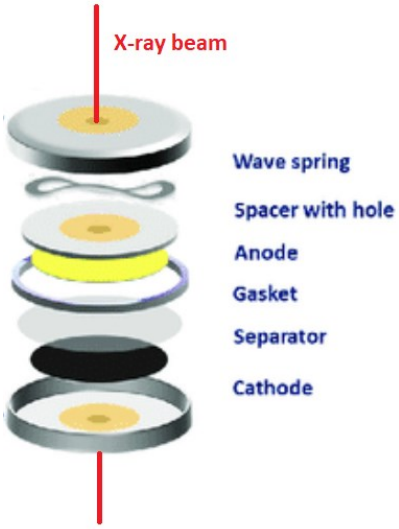
Sequential refinement by the Rietveld Method of an *operando* electrochemical cell with phase separating $LiFePO_4$ battery material with FullProfAPP.

In this exercise we will show an *operando* X-ray diffraction measurement of an electrochemical cell that contains $LiFePO_4$ as the active material. The experiment was carried out at the new NOTOS beamline at ALBA synchrotron ($\lambda = 1.12698$ Å) in the 11.1º – 60.0º 2θ range. The modified coin cells were cycled in galvanostatic mode (constant current) with a rate of C/7.

This is a typical scheme of an operando electrochemical coin cell using a kapton window. The experiment is carried out in transmission mode.



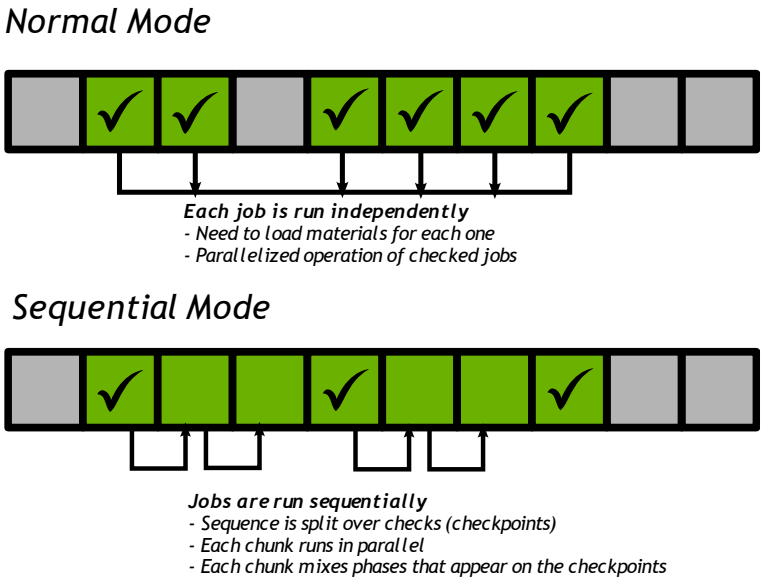
An *operando* X-ray diffraction experiment of an electrochemical cell follows the evolution of the active material ($LiFePO_4$ in this case) upon oxidation and reduction, for a certain current applied within some potential limits. Under normal operation conditions, $LiFePO_4$ is known to be a phase separating material. This means that upon oxidation (lithium deintercalation), a new phase $FePO_4$ with a very similar crystal structure, starts to nucleate, increasing its phase fraction. The reverse process of reduction (lithium intercalation) is expected to happen in an analogous way. This means that phases with intermediate compositions are not stable with respect to the formation of the edge $LiFePO_4$ and $FePO_4$ phases and should not be visible in our diffractograms.

The experimental data is provided in **'Examples/LiFePO4/LiFePO4_14LFPKa',** an instrumental resolution function is also provided in **'Examples/LiFePO4/IRF_NOTOS_July2022_MR.irf'**.

Exercise:

1. Select the **'Examples/LiFePO4/'** 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. Looks like something went wrong with the first two patterns, doesn't it?

4. Considering point 3**, Check** the appropriate patterns for the analysis using the 'Pattern Checks' option. Remember Monday's lecture, 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).



5. Use the app to extract the **background** points, pay special attention to the 12.0º – 18.0º 2θ region.
6. **Download CIF** files from the Crystallographic Open Database using the app's client. Remember that we are dealing with a phase separating material. Additionally, the *operando* cell also contains a **highly textured Aluminum** foil (current collector) which does not meet the powder diffraction criteria (some crystallographic planes are over-represented with respect to others).
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. Remember that the Aluminum signal is highly textured. Take care of the artifact appearing on the first datapoint of the patterns by excluding it from the refinement.
10. Perform the **sequential refinement**. Look at the results. Do you see the **nucleation of the $LiFePO_4$ and $FePO_4$** phases upon oxidation and reduction?