Using on-the-fly Rietveld analysis to follow in situ synchrotron X-ray powder diffraction experiments in real time

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For most compounds, high resolution powder diffraction patterns of samples at modern synchrotron beamlines are collected within seconds. These acquisition times will further decrease by more than an order of magnitude as synchrotrons undergo upgrades to increase beam flux. For \textit{in situ} or \textit{operando} studies tens of thousands of patterns can be collected on a single reaction within a single day. For these \textit{in situ} reactions the only way of evaluating experimental progress is by following structural changes from resulting 1D patterns via visual inspection. Without distinct structural changes to the reactants within the system to indicate a reaction’s completion it is on the user to make their best estimate on when they have collected enough data. These worries often lead to overcollection on the sample to ensure desired outcomes are met.

To combat these issues plaguing \textit{in situ} and \textit{operando} experiments, we created a Python code to run Rietveld refinements on collected patterns \textit{on-the-fly}. The typical Rietveld analysis is finished within days to years after the experiment completion while the software does not replace this process it provides a first look at the structure changes \textit{in real time}. Existing refinement (TOPAS \cite{1}) and integration (pyFAI \cite{2}) software enabled the rapid analysis leading to a full structural determination within seconds of a pattern’s acquisition collection. This allows the user to make informed decisions on the experiment at hand. An example is given below where ion exchange \cite{3} was impossible to follow by the 1D patterns, yet had clear kinetic rates were determined from the on-the-fly refinements. This software has been tested at the Advanced Photon Source, National Synchrotron Light Source II, and Stanford Synchrotron Radiation Lightsource powder diffraction beamlines. On-the-fly Rietveld analysis is an important step in creating structure informed autonomous beamline experiments.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{1D diffraction patterns taken by synchrotron diffraction of the intermediate Na\textsubscript{x}Li\textsubscript{1-x}Mg\textsubscript{2}P\textsubscript{3}O\textsubscript{9}N phase 301 and 311 peaks during ion exchange (left). The reaction progression is indicated by a peak shift for a lattice parameter change <0.1%, impossible to see by eye. Using on-the-fly Rietveld analysis (right) not only was the reaction followed, but a kinetic rate with an R\textsuperscript{2} > 0.985 was determined for the ion exchange reaction based on the peak shifts within the first two hours.}
\end{figure}


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