Considerations for quantitative in situ X-ray powder diffraction studies of solid-state reactions

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The importance of sample preparation in collecting high-fidelity powder diffraction data suitable for quantitative structure and phase analysis is well established. Such powder diffraction experiments are increasingly being applied in situ, during reactions, to explore solid-state reactivity. When applied in situ, X-ray diffraction is widely used to gain insight into the mechanism and kinetics, and to identify dynamic intermediate states. Here, using a model ion-exchange reaction (NaFeO₂ + LiCl → LiFeO₂ + NaCl), we show that sample preparation not only influences the fidelity of powder diffraction analysis but also impacts the observed reaction progress. Specifically, we found that the observed reaction progress can differ by ~50% depending on the capillary sample preparation. Thus, for in situ diffraction studies of solid-state reactions, packing fraction is an important and previously unrecognized consideration that impacts reproducibility and fidelity of the reaction study.

1. Introduction

Quantitative phase analysis of powder X-ray diffraction (PXRD) data collected in situ, as a reaction occurs, is increasingly being used to evaluate how the abundance of reagent, intermediate and product phases evolve and to gain insight into the reaction kinetics and mechanism. By comparing how a reaction evolves at different temperatures, with different chemical precursors and for different stoichiometries, we can develop an understanding of what governs reaction progress (Agca et al., 2020; Chen et al., 2011; Wu et al., 2015) so that, ultimately, we can design reactions that deliver new target materials with optimal yield, purity and cost (Wicker & Walker, 2013; Martinolich et al., 2016; Todd et al., 2020; Shoemaker et al., 2014).

Widespread efforts have been invested in developing X-ray-compatible reaction environments (Chupas et al., 2008; Borkiewicz et al., 2012; Liu et al., 2016; O’Nolan et al., 2020; Beauvais et al., 2022) to control reaction conditions (e.g. temperature, gas environment, electrochemical state) accurately and precisely to ensure that these in situ experiments deliver reproducible insights that are reflective of the system being studied, and not how the experiment was undertaken. This includes accurate heating, precise reaction initiation and reliable electrochemical cycling.

Naturally, high-fidelity in situ studies also take into account best practices for acquisition of quantitative X-ray characterization data (Ermrich & Opper, 2013; Buhrke et al., 1997). For PXRD data for quantitative Rietveld analysis, these include avoiding preferred orientation effects (i.e. having good ‘powder averaging’), ensuring that the sample absorption is below a critical threshold and ensuring good signal-to-noise ratio, amongst others; these are critical considerations in

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sample preparation and are optimized on the basis of packing fraction, packing techniques, capillary diameter and the use of diluents.

Recently, we have found that the kinetics and reaction progress of solid-state reactions can depend strongly on the density of the reagent packing (Kamm et al., 2022). Here we demonstrate the substantial differences in reaction progress that can occur due to different packing of a mixture of reactive powders into capillary-based in situ reactors. For a model ion-exchange reaction \( \text{NaFeO}_2 + \text{LiCl} \rightarrow \text{LiFeO}_2 + \text{NaCl} \), we see that the observed relative reaction progress can differ by \( \sim 50\% \) depending on the capillary sample preparation. Thus, in studies of solid-state reactions, the packing fraction is an important and previously unrecognized consideration that impacts the reproducibility of the reaction study, as well as comparisons between different reaction conditions or reactions in the laboratory versus at the beamline versus in different reactor environments.

2. Experimental

The topotactic ion-exchange reaction \( \text{NaFeO}_2 + \text{LiCl} \rightarrow \text{LiFeO}_2 + \text{NaCl} \) was selected as a model because it does not involve changes in structure or crystal volume. \( \text{Na(Li)}\text{FeO}_2 \) has an \( \text{R3m} \) structure formed by layers of edge-sharing \( \text{FeO}_6 \) octahedra with Na\(^+\)/Li\(^+\) intercalated between the layers. \( \text{Li}(\text{Li}/\text{Na})\text{FeO}_2 \) is a rock salt phase (\( \text{Fm3m} \)).

The reaction mixture was prepared by mixing \( \text{NaFeO}_2 \) (McAuliffe et al., 2023) and \( \text{LiCl} \) (AlfaAesar, ultradry 99.999\% pure) in a 1:2 molar ratio in an inert atmosphere glovebox. To emulate the different powder packing densities that can be achieved for capillary-loaded samples, some of the reaction mixture was tamped inside the capillary (0.9 mm inner diameter, borosilicate, one end closed) and some was allowed to fall into the capillary without applying additional force. Glass wool was inserted into the capillary to secure the powder. The capillary was sealed, heated at 310°C in a muffle furnace for 1 h and recovered to room temperature to map the reaction progress at different points along the capillary. A large metal block inside the oven was used to minimize temperature non-uniformities.

Spatially resolved X-ray diffraction data were collected along the reacted capillary, at positions separated by 0.64 mm, using a Bruker D8 diffractometer equipped with a focused Mo source (0.5 mm collimator, \( \sim 0.5 \times 0.5 \text{ mm beam size} \)) and an Eiger2R area detector. Data were reduced using the Bruker \textit{DIFFRAC.EVA} software package (https://www bruker.com/eva; Bruker AXS, Karlsruhe, Germany) and the scattering contribution from the glass capillary was subtracted. A NIST silicon standard was used to quantify the instrumental parameters. Quantitative phase fractions were derived from Rietveld refinement of multi-phase models against the data within \textit{TOPAS Academic v6} software (Coelho, 2018).

3. Reactivity depends on the powder-packing density

The sum of the scale factors from the Rietveld refinement of the multi-phase model against the data varies across the sample, reflecting the non-uniform sample powder packing density (Fig. 1). The progress \( (p) \) of the reaction \( \text{NaFeO}_2 + \text{LiCl} \rightarrow \text{LiFeO}_2 + \text{NaCl} \) was quantified on the basis of the scale factor (and relative molar quantities) of \( \text{LiFeO}_2 \) and \( \text{NaFeO}_2 \) at each position across the capillary \( [i.e. \ p = \text{mol} \ \text{LiFeO}_2/(\text{mol} \text{NaFeO}_2 + \text{mol} \text{LiFeO}_2)] \). The reaction progress directly mirrors the changes in sample powder packing, varying by \( \sim 50\% \) across the capillary \( (p_{\text{min}} = 0.35, \text{cf}., p_{\text{max}} = 0.52 \text{ after 1 h at 310°C}) \). Thus, the progress of the reaction can be correlated to the powder packing density. Where the reaction mixture was more densely packed due to tamping during sample loading or the insertion of glass wool, the reaction is more complete; where the reactive mixture was less densely packed, the reaction is less complete.

Computational modelling suggests that this difference in reactivity can be attributed to the change in the number of reactive neighbouring particles as the powder packing is changed (Kamm et al., 2022). For higher-density powder packing, there are more reactive neighbours, and shorter transport pathways, so the reaction progresses further. Although the impact of packing density is straightforward for this topotactic ion-exchange reaction, more complex behaviours are anticipated for solid-state reactions involving significant structural re-arrangements and changes in the crystal volumes for the products compared with the reagents.

4. Impact on in situ X-ray diffraction studies of reactions

Although best practices for loading sample capillaries aim to distribute powder uniformly (Dean & McIntyre, 1999; Von Dreеле, 2006) with respect to the particle orientation to...
also report the powder packing density. Experiments exploring reactivity and reaction kinetics should contribute to inconsistent observations for the same reaction (Baker, 2016). The reproducibility and comparability of measurements can be improved by deliberately controlling for packing density (i.e. the volume fraction occupied by reactive particles). The powder packing density, and uniformity thereof, can be established from an X-ray absorption scan across the sample, normalizing for the sample geometry and absorption (Dreele et al., 2013). Alternatively, a known uniform packing density may be achieved by pressing the reaction mixture into a pellet that is then roughly broken up and loaded into the capillary; the local density of the reactive particles (as is relevant to the reaction progress) is determined by the packing density of the pellet. This approach may more closely match how some solid-state reactions are carried out in the laboratory and, therefore, may yield more directly comparable results. Ensuring a uniform packing density is vital to experiments that rely on spatial mapping, such as those using a thermal gradient reactor (O’Nolan et al., 2020; Wustrow et al., 2021, 2022), to ensure that the trends observed are solely due to temperature and not differences in powder packing. To facilitate comparisons between different studies, experiments exploring reactivity and reaction kinetics should also report the powder packing density.

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