

2.9. Cells for *in situ* powder-diffraction investigation of chemical reactions

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2.9.1. Introduction

In a time-resolved powder-diffraction experiment performed *in situ* (sometimes also called non-ambient diffraction), the aim is to follow the behaviour of a sample as a function of one or more external stimuli. The use of this technique can be roughly divided into two fields: academic research and industrial applications. In academic research, the goal is generally to understand the structure–property relationship of the studied material and then to use this understanding in order to improve the design of materials, pharmaceutical products, synthesis routes, reaction conditions *etc.* In the industrial world, one typically wants to learn whether a particular phase, phase mixture or polymorph arrives at a certain time in a production process. Reaction cells that are well suited to industrial applications may well be inadequate for academic research and *vice versa*. Owing to the huge variety of applications, it is impossible to come up with a generic cell design. In this chapter, we show what information content is accessible for a given combination of X-ray or neutron source and *in situ* cell through various case studies. The enabling technology that has driven these recent developments will be outlined in the next section, followed by an overview of the different types of reaction cells in use at home laboratories and at synchrotron and neutron facilities. Finally, we indicate some areas in which new developments can be expected.

2.9.2. Historical perspective

Within a decade of the discovery of the Bragg law, Westgren & Lindh (1921) had already observed several different polymorphs of iron as a function of temperature using powder diffraction. We have recently celebrated the centenary of the founding of X-ray crystallography, and during this time the use of *in situ* powder diffraction has become immensely popular. Although most of the pioneering powder-diffraction experiments were performed with X-ray tubes and scanning point detectors or with neutrons and an array of detectors, the real breakthrough came with the advent of synchrotron sources, providing high-energy penetrating X-rays, in combination with area detectors. This combination of source and detector type allowed diffraction experiments to be performed with both good angular and time resolution, thus opening up many new applications in chemical, physical, material and biological sciences. The topic of *in situ* cells for chemical reactions is therefore an enormous field and we cannot claim to provide an exhaustive list of instruments. We rather intend to point out the major cell designs, and to provide the reader with an overview to allow them to select the appropriate device for their application and available diffraction apparatus. We have tried to select where possible *in situ* case studies that use the full power of crystallography by solving structures and/or performing Rietveld refinements. A large number of review articles and book chapters written by some of the pioneers in this field have appeared during the last two decades with some overlap but slightly different emphasis. Walton & O'Hare (2000) describe many aspects of the crystallization of inorganic solids. Norby (2006) looks at zeolite synthesis, including an excellent commented reference list. Evans

& Radosavljević Evans (2004) focus on what can be performed with conventional equipment available in many university departments. Majuste *et al.* (2013) illustrate reactions relevant to hydrometallurgy studied with *in situ* synchrotron X-ray diffraction (XRD). Parise *et al.* (2000) also concentrate on synchrotron-based examples, and already foresee the abundance of data coming from modern third-generation powder-diffraction beamlines. Automated analysis tools are still underdeveloped, and we will comment on possible future developments in this area. Norby & Schwarz (2008) discuss powder diffraction under non-ambient conditions using X-ray sources, cells and diamond-anvil cell work. *In situ* gas–solid reactions are discussed by Møller *et al.* (2014), and Sharma *et al.* (2015) review the rapidly growing field of crystallographic–electrochemical investigations for both X-rays and neutrons. References to review articles for neutrons are given below (see Section 2.9.3.4).

2.9.3. Main types of reaction cells

2.9.3.1. Introduction

Powder-diffraction experiments can be performed either in transmission or reflection geometries. The diffraction signals can be collected in angular- or energy-dispersive mode with parallel or focused X-ray or neutron beams. Dedicated reaction cells have been developed for all possible permutations of the above variables. Each setup has its own trade-off in terms of time, angular and crystallographic resolution, and intrinsic limitations in data quality. In the last two decades, enormous progress has been made in instrumentation for diffraction experiments. A good example is the development of X-ray detectors where, as a direct consequence of the use of linear or area detectors, a time resolution of seconds or even shorter is now feasible in angular-dispersive mode. These and many other developments, such as more intense laboratory X-ray sources, have redefined the ways in which one can best perform *in situ* experiments. Energy-dispersive systems have lost some of their early advantages with respect to angular-dispersive geometries; nevertheless, there are still good grounds for selecting the energy-dispersive technique for some applications. Similarly, reflection-geometry flat-plate reactors have lost a lot of their early popularity because of well known problems with the diffraction geometry during heating. On the other hand, flat-plate strip heaters can reach thermal ramp rates that are hard to obtain otherwise. Flat-plate reflection-geometry reactors remain the main workhorses in academic and industrial home laboratories (mainly because of the good diffraction intensities which they provide) and several commercial vendors sell these units. Commercial and home-laboratory-developed cells, such as that from Moury *et al.* (2015) for high-pressure hydrogenation experiments, often provide the basis for further studies at central facilities. In this chapter, we intend rather to focus on new types of cells and their use with modern linear and area detectors, also indicating the level of information that can be obtained. Microreactors in the form of capillary cells are popular for many different kinds of *in situ* diffraction experiments, and we therefore will review their use in some detail.