

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

W. VAN BEEK AND P. PATTISON

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.

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2.9.3.2. Capillary cells

Capillary cells, also called microreactors, exist in many variations. Depending on the application (temperature, pressure and chemical environment), capillaries may be made of polyimide, glass, quartz, single-crystal sapphire or steel. They are simple and extremely efficient devices which can accommodate a large number of different applications. The impetus for their development has mainly come from catalysis research, but they have also been successfully employed to perform *in situ* reactions on intercalation, ion exchange, gas sorption/desorption, cement hardening, hydration–dehydration, light-induced transitions, crystallization processes and polymorphism, to name a few. Capillary cells are almost always used together with temperature- and/or gas-handling (static pressure or flow) devices. In open geometry, or with simple heat shields, one can easily obtain

temperatures ranging from 80 to 1000 K with cryogenic and hot-air blowers or resistive heaters close to the sample. Static gas pressures can be as high as 30 MPa and in flow cells 2 MPa is commonly reached, as well as vacuum conditions. Capillary cells were first applied by Clausen (1991) and have been adapted numerous times (Brunelli & Fitch, 2003; Chupas *et al.*, 2008; Jensen *et al.*, 2010; Madsen *et al.*, 2005; Norby *et al.*, 1998, 2000; Palanchar *et al.*, 2005) together with gas-handling systems (Eu *et al.*, 2009; Hill, 2013; Krogh Andersen *et al.*, 1998; Llewellyn *et al.*, 2009), with large 6 mm-diameter samples (Andrieux *et al.*, 2014), with supercritical solvents up to 40 MPa with a swing-in blower for rapid heating (Becker *et al.*, 2010) or with pulsed supercritical flows (Mi *et al.*, 2014) for following synthesis reactions. A recent review of several capillary cells for high-pressure reactions (Hansen *et al.*, 2015) also contains useful information on how to calculate burst pressures.

One of the most critical issues is how to create a reliable leak-tight connection between the capillary and the metallic or polyether ether ketone (PEEK) gas/liquid supply line(s). For fragile capillaries there are basically two strategies: either to glue the capillary to a metal support with high-temperature epoxy (see Fig. 2.9.1), or to use ferrules. When both ends of a capillary have to be tightened with thin-walled capillaries, the use of ferrules needs some skill (see Fig. 2.9.2).

If the working temperature permits, it is easy and reliable to use a stainless-steel bracket in which capillaries are glued such that all mechanical forces are transferred to the support instead of being taken up by the thin (glass) capillaries (van Beek *et al.*, 2011), as in Fig. 2.9.3. Gas systems are typically constructed from a combination of pressure reducers, mass-flow meters, valves and a manifold which supplies gases to the cell at controlled pressures and flow rates. It is worth pointing out the less-common back-pressure regulator used in Fig. 2.9.3. This unit allows 2 MPa of pressure to be maintained on the sample during flow experiments. Backpressure regulators for much higher pressures are commercially available, but these have so far not been used for *in situ* work. *In situ* diffraction has been coupled with stable-isotope analysis to correlate isotope fractionation with crystal structure. For this, a nonmetallic flowthrough capillary cell that avoids any contamination from the components of the cell itself was designed (Wall *et al.*, 2011). Many hundreds of studies have been performed over the last two decades with capillary devices in the above-mentioned fields.

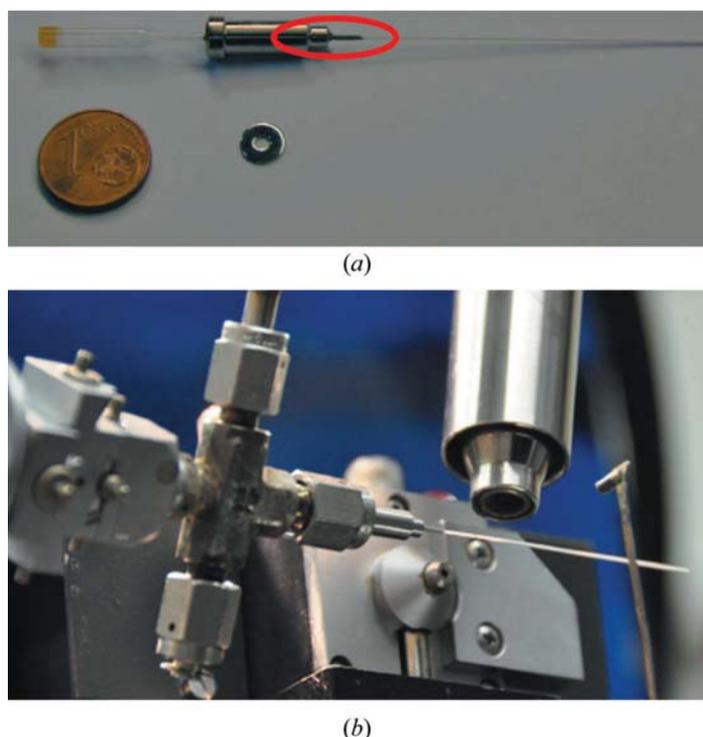


Figure 2.9.1
(a) Swagelok VCR gland with an epoxy-glued capillary (red ellipse). (b) VCR capillary cell on a beamline with a cryostream (adapted from Jensen *et al.*, 2010).

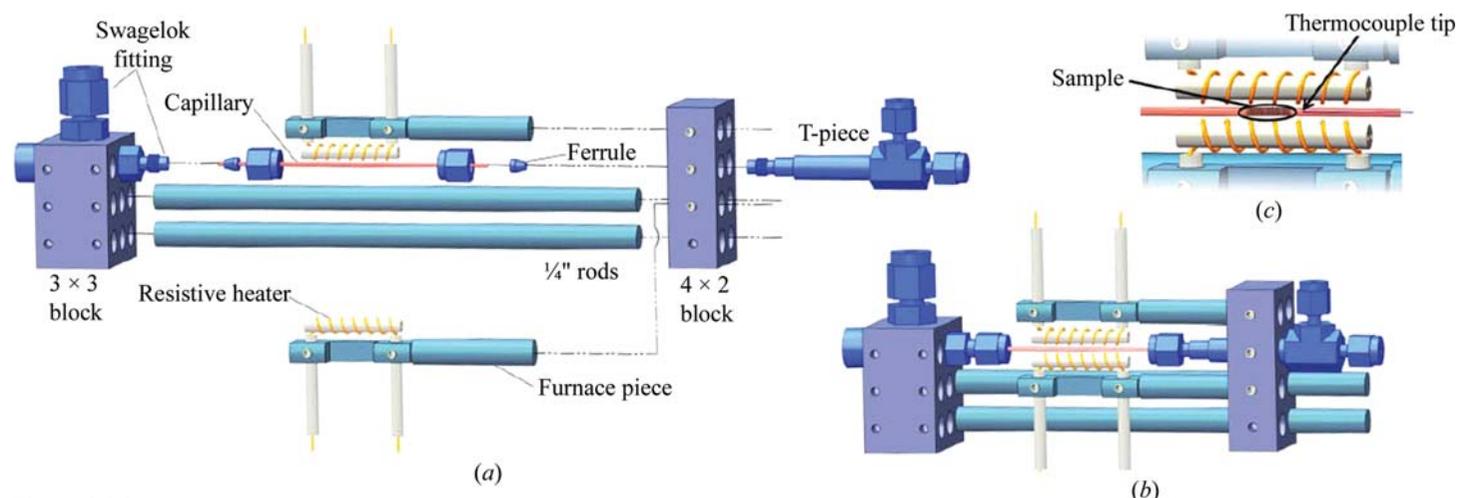


Figure 2.9.2
(a) An exploded representation of the flow-cell/furnace components, indicating how they fit together. (b) The fully assembled flow cell/furnace. (c) An expanded view of the sample region, indicating the relative position of the sample and thermocouple tip within the furnace hot zone (adapted from Chupas *et al.*, 2008).

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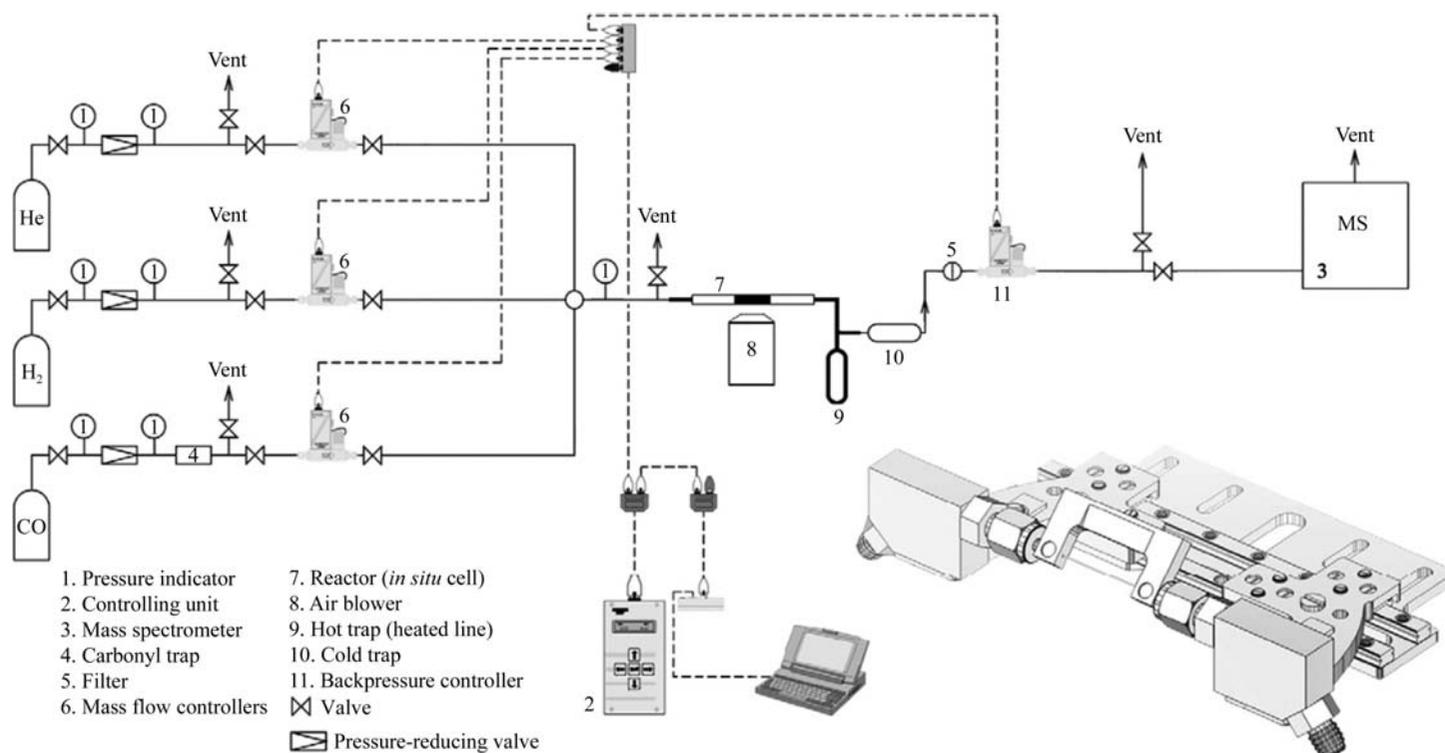


Figure 2.9.3

Sketch of a typical experimental setup and a three-dimensional drawing of the *in situ* flow cell. Note the strain-relief bracket over the capillary. Adapted from Tsakoumis *et al.* (2012), with permission from Elsevier.

Above 800 K, open capillary systems have severe heat loss and the use of insulation or reflectors around the sample or mirror furnaces is more appropriate. See Lorenz *et al.* (1993), Margulies *et al.* (1999), Proffen *et al.* (1995), Riello *et al.* (2013) and Yashima & Tanaka (2004) for special designs to minimize heat loss. Finally, it is worth mentioning the recent work of Figueroa *et al.* (2013), which combines the strong points of the various capillary designs, and also work by Johnsen & Norby (2013), who managed to create and study a working battery in a capillary.

In any powder-diffraction experiment (Warren, 1990), but particularly when using capillary cells, the experimentalist needs to take special care in order to obtain sufficient averaging in terms of grain statistics and to avoid preferred orientation. Typically *ex situ* capillaries are spun, but when gas lines are attached to the sample, spinning is not possible and only rocking or stationary geometry can be used. In addition, a fine (ground) polycrystalline powder giving perfect homogenous Debye-Scherrer rings, even without spinning, often results in an excessive pressure drop due to its high density and packing. In such cases, the sample may need to be pressed into a pellet and then crushed again to obtain larger agglomerates that allow sufficient gas flow through the sample (Jacques *et al.*, 2009). However, relatively large agglomerates, while reducing the packing density, might still give nonhomogeneous powder rings, which affects the intensities, especially on one-dimensional detector systems (strip detectors or crystal-analyser high-resolution systems). For all of these reasons it is not always straightforward to acquire reliable intensities under *in situ* conditions. If, however, proper care is taken, then precise structural parameters can indeed be refined from *in situ* data. For example, Milanese *et al.* (2003) obtained a detailed view of the structural rearrangements induced by the template-burning process from 350 to 1000 K on a zeolitic MFI framework. Oxygen flowed through a rocking sample and diffraction data were collected on a translating two-dimensional image plate capable of verifying the reliability of the measured

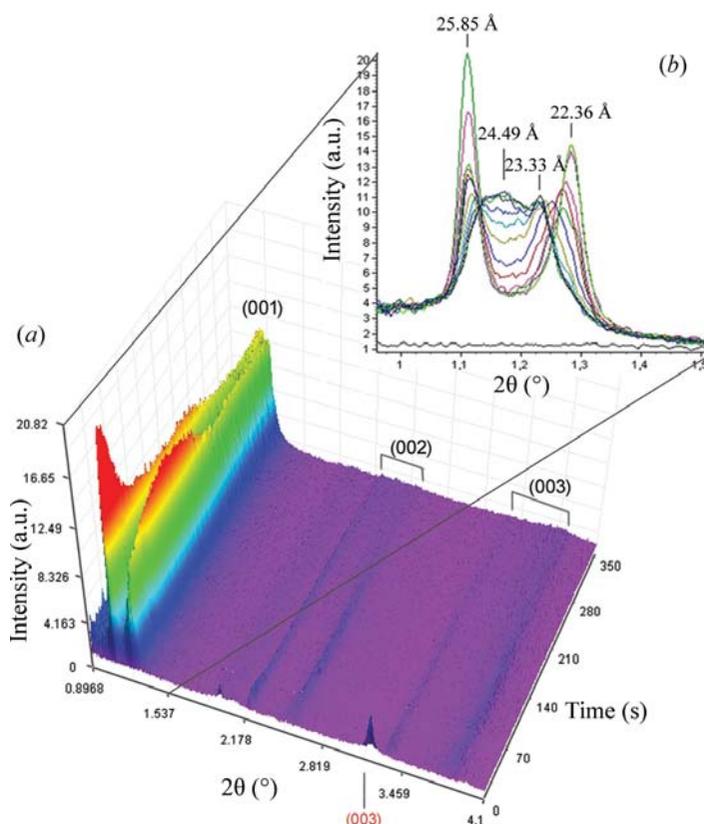


Figure 2.9.4

(a) *In situ* three-dimensional stacked plot of the intercalation of ibuprofen into an LDH. Miller indices are shown in black for the intercalation product peaks and in red for the LDH nitrate starting material peaks. (b) Two-dimensional patterns showing the low-angle peaks during the first instance of the reaction. Adapted with permission from Conterposito *et al.* (2013). Copyright (2013) American Chemical Society.

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intensities with a time resolution of several minutes (Meneghini *et al.*, 2001). From the temperature-dependent *in situ* data, the authors were able to extract the overall template occupancy in the framework. This allowed a definition of the key steps in the template-removal process, namely the start of the template decomposition, the start of the template burning and the end of the template burning. These three steps were then used to explain the cell-parameter evolution and atomic displacement parameters of the Si-framework atoms. Kinetic analysis performed on the results from the Rietveld refinements suggested a diffusion-limited reaction of the volatile products of the template leaving the framework (Milanesio *et al.*, 2003).

Conterosito *et al.* (2013) reduced the time resolution to 100 ms per image using a Pilatus 300 K-W (Kraft *et al.*, 2009) pixel detector installed on an ESRF bending-magnet beamline in combination with a capillary reactor. In these experiments, a mechano-chemical method for fast and clean preparation of exchanged layered double hydroxides (LDHs) was investigated. The inorganic anion in the interlayer region (chloride or nitrate) was exchanged with a series of organic pharmaceutically important molecules. In Fig. 2.9.4, one can see the diffraction patterns of the intercalation process of ibuprofen into an LDH, which allowed the complex mechanism to be understood. Firstly, it is striking to note that the signal from the LDH starting material (the 003 reflection, in red) decreases, while the products and intermediates (001 reflections in black) grow already immediately after the first 100 ms image. Secondly, one can see that the low-angle peaks ($<1.5^\circ$) show a different behaviour in time, suggesting a two-stage process with an intermediate phase and, thirdly, one sees that the intercalation process is over in ~ 4 min. The reliability of the *in situ* procedure was confirmed by comparing the production yield of *ex situ* and *in situ* experiments. Owing to the complex two-stage process, kinetic analysis was not possible in the case of ibuprofen. In the same article, however, it was shown that it was possible to perform a full kinetic analysis on single-stage intercalation processes with different molecules reacting at comparable speeds. It is hard to imagine that so much detail on such timescales could be obtained using other techniques. For example, related intercalation experiments performed with energy-dispersive diffraction (Williams *et al.*, 2009) were, at that time, still limited to 10 s per pattern. Hence it was not possible to study the kinetics of such fast intercalation processes by other means.

Care must be taken to ensure that, when performing experiments at microgram or microlitre levels inside capillaries, the results are still representative of the bulk reaction. Therefore, when studying *in situ* catalytic reactions, it has become common practice to measure the activity or selectivity of the sample with gas chromatography or mass spectrometry (see Fig. 2.9.3) at the same time. It is also well known from reactor engineering that pressured drops, diffusion effects and flow disturbance are important parameters to take into account (Nauman, 2008). The term *operando* was introduced by Bañares (2005) during a discussion with colleagues (Weckhuysen, 2002) for these combined experiments coupling structure with the sample activity.

If the miniaturization turns out to be problematic, one could consider measuring bulky (~ 1 cm or more) samples and/or using larger reaction vessels in combination with either energy-dispersive diffraction or extremely high X-ray energies (Tschentscher & Suortti, 1998). This gives the additional advantage that identical sample volumes to those for neutron studies can be used. Hence, one often needs to utilize reaction

cells that are specifically designed for the application, as explained in the following section.

2.9.3.3. Reactions requiring specialist cells

2.9.3.3.1. Cells for electrochemistry

With ever-increasing standards of living, the world is becoming more and more dependent on energy. As natural resources (coal, gas and petrol) are limited, there has been a large impetus towards developing alternative ways of producing and storing energy, while also taking into account environmental issues. Despite many decades of research and tremendous progress in

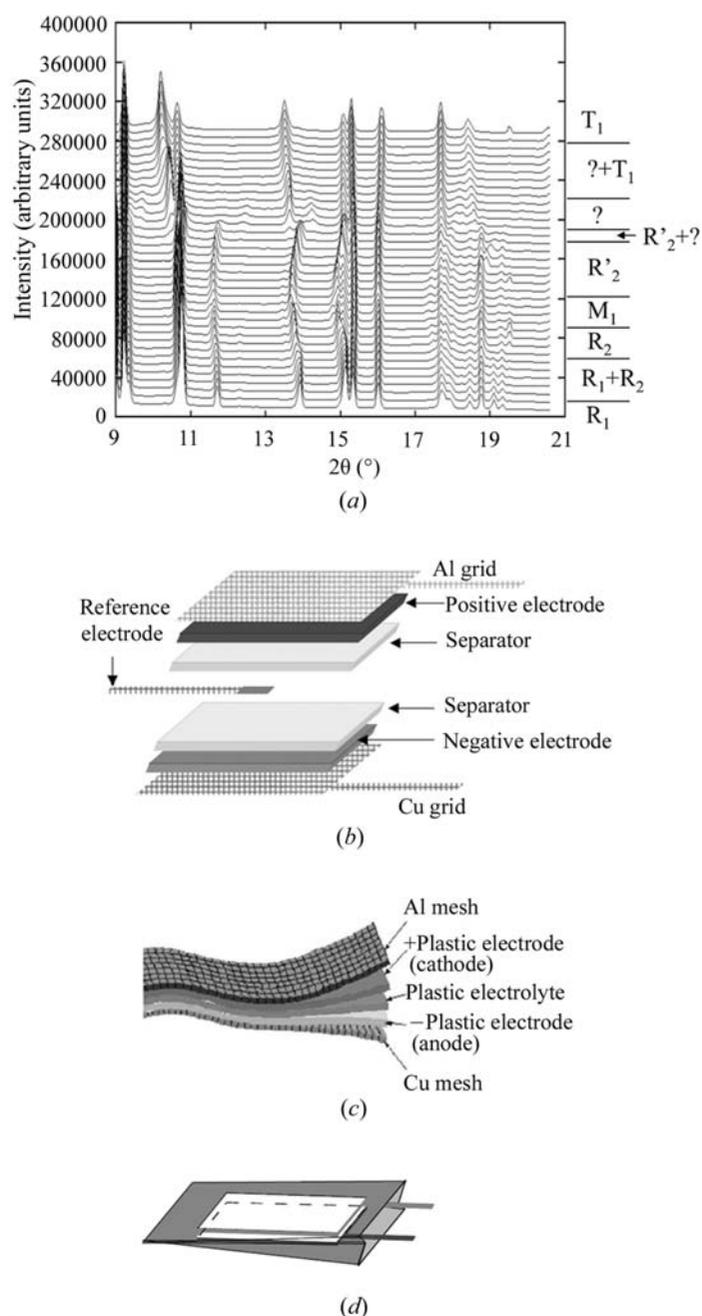


Figure 2.9.5

(a) *In situ* synchrotron diffraction patterns (selected region) of an LiCoO_2/Li cell collected during cell charging. Below: overview of a Bellcore flat three-electrode plastic Li-ion cell (b) with an enlargement (c) of the assembly steps during which all the separated laminates are brought together by a thermal fusion process *via* a laminator. The thicknesses of the plastic Li-ion cells assembled for *in situ* X-ray experiments were about 0.4/0.5 mm. A derived version of the Bellcore plastic Li-ion battery with a beryllium window thermally glued to the packing envelope on one side is shown in (d). Adapted from Morcrette *et al.* (2002) with permission from Elsevier.

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this field, *in situ* diffraction was only adapted for electrochemical research in the 1990s. Nevertheless, this field now has the largest variety of cells. It is impossible to give a comprehensive overview of this complex subject here, and therefore the reader is referred to the articles by Brant *et al.* (2013), De Marco & Veder (2010) and Morcrette *et al.* (2002), which describe how to design and reference most existing miniaturized *in situ* cells. The recent work by Johnsen & Norby (2013), who have developed a capillary-based micro-battery cell, is not included in these reviews. The main advantage of this cell is that it allows diffraction data to be obtained from a single electrode. The recent work on electrochemical cells using conventional diffractometers (Shen *et al.*, 2014) and high-throughput cells for synchrotron applications (Herklotz *et al.*, 2013, 2016) is also relevant. When planning experiments on central facilities, not only appropriate cells but also dedicated ancillary equipment (*e.g.* a glove box) for cell loading owing to air sensitivity of the electrode material (*e.g.* lithium) are essential. In centralized facilities, this may lead to conflicts due to the incompatibility of liquid electrolytes with samples from other users, and dedicated electrochemistry glove boxes have started to appear. As an example of the use of an electrochemical cell, Morcrette *et al.* (2002) managed to perform structural Rietveld refinement during delithiation of an LiCoO_2 electrode. In order to obtain reliable intensities, five diffraction images at six different positions in the cell were averaged for each point in the charge cycle. Owing to the amount and quality of the data, six different structural phases could be determined, including lattice parameters, space group, atomic positions and *R* factors (see Fig. 2.9.5). As the potentiostat or galvanostat is driving and measuring the performance of the battery, the structure–activity relationship is obtained automatically. This is a similar concept to the *operando* methodology in catalysis research that uses a mass spectrometer to measure activity.

In analogy with microcapillary cells, miniaturized electrochemistry cells are extremely efficient for studying many aspects of an operational battery despite the fact that a fundamental understanding of electrochemical systems is inherently challenging. All the components of a cell influence each other at the interfaces during the cyclic charge-transfer process. It is also crucial to be able to establish the critical factors that determine the lifetime of the battery. To make efficient use of beamtime, it is common practice to construct many cells within one frame, all operating in parallel. The whole batch of cells is then mounted on translation stages on a diffractometer and measurements are taken periodically. However, miniature cells will never provide a complete picture, and there will always be a need to study large prototype or production cells (Rijssenbeek *et al.*, 2011) of the types discussed in Sections 2.9.3.3.3 and 2.9.3.4.3.

2.9.3.3.2. Cells with humidity control

Humidity is a relevant parameter in many areas of research. For instance, the interlayer spacing in clays, corrosion, pharmaceutical processes, cement hardening, phase transitions in minerals or proton conductors and crystal growth of salts are all dependent on relative humidity, often in combination with high temperatures.

Most work so far has been carried out in home laboratories with flat-plate commercial chambers connected to a manifold with a gas mass-flow controller and liquid mass-flow controllers, thus providing an air flow with controlled humidity (Chipera *et al.*, 1997; Kühnel & van der Gaast, 1993; Watanabe & Sato, 1988). In addition, capillary cells have also successfully been used

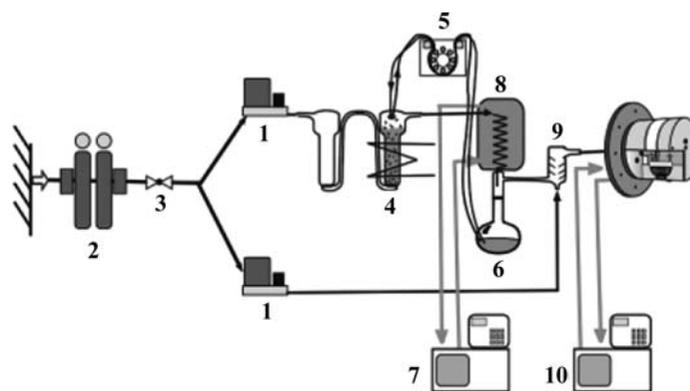


Figure 2.9.6

Schematic drawing of the humidity-control system: (1) mass-flow controller, (2) adsorption dryer, (3) pressure regulator, (4) heated bubbler, (5) peristaltic pump, (6) water reservoir, (7) thermostat, (8) condensation trap, (9) mixing chamber and (10) thermostat. Adapted with permission from Linnow *et al.* (2006). Copyright (2006) American Chemical Society.

(Walspurger *et al.*, 2010) on synchrotrons. It is imperative to have very good thermal stability and to avoid temperature gradients throughout the system. The dew point of water is strongly affected by temperature, and unwanted condensation of water can easily occur on colder parts of the system. Fig. 2.9.6 shows a schematic of a humidity-control system developed by Linnow *et al.* (2006). The thermal management in this design has been optimized to avoid condensation.

Linnow *et al.* (2006) and Steiger *et al.* (2008) have used the system in Fig. 2.9.6 to investigate the crystal growth of various salts, which is considered to be the cause of many failures in building materials (stone, brick, concrete). In order to do so, they scanned through the relative humidity (RH) *versus* temperature phase diagrams of these salts in various porous materials used in the building industry. Diffraction experiments revealed differences in reaction pathways and stress in both host and guest materials.

The NASA Phoenix Mars Lander has discovered perchlorate anions on Mars. This is important, since they could possibly be used as indicators for hydrological cycles. Robertson & Bish (2010) studied a magnesium perchlorate hydrate system, $\text{Mg}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$, with the aim of solving the various unknown crystal structures as a function of water content *n*. Fig. 2.9.7 shows *in situ* diffraction data collected during dehydration in a

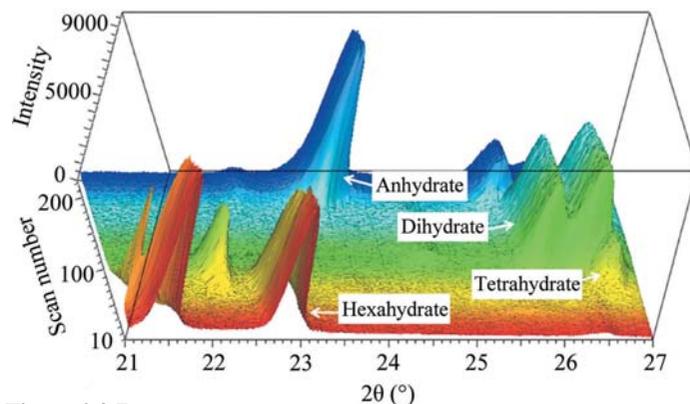


Figure 2.9.7

Sequence of XRD measurements between 21 and 27° 2θ . On heating at a rate of 2°min^{-1} at $<1\%$ RH, sequential dehydration was observed, with the anhydrate observed at the highest temperature. The vertical axis represents intensity. The ‘time’ (scan number) axis represents temperature from 298 to 498 K in 2°min^{-1} increments. Adapted from Robertson & Bish (2010).

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commercial Anton Paar flat-plate heating stage connected to an automated RH control system similar to that shown in Fig. 2.9.6. The rapidly collected *in situ* data (30 s per scan, with a position-sensitive detector) were crucial to define at what temperatures longer data collections had to be taken in order to acquire single-phase, high-quality powder patterns suitable for crystal structure solution. Robertson & Bish (2010) managed to index and solve the dihydrate and tetrahydrate phases by charge flipping. Although the tetrahydrate structure was later revised by Solovyov (2012) using the exact same data, this example clearly indicates the level of complexity that can be studied in local laboratories under *in situ* conditions. In this case, this task included understanding the dehydration pathway, solving the structure of $\text{Cl}_2\text{H}_4\text{MgO}_{10}$ with two molecules in the unit cell and refining anisotropic displacement parameters using Rietveld refinement.

2.9.3.3.3. Large-volume cells for energy-dispersive diffraction

Large-volume cells have been used to date with great success almost exclusively with energy-dispersive diffraction (EDXRD). Early work on this was carried out by Munn *et al.* (1992) and He *et al.* (1992) using the synchrotron source at Daresbury Laboratory. Walton & O'Hare (2000), who continued the pioneering work, provide a good historical overview of the kinds of studies that can be performed. Norby (2006) also provides excellent references to and explanations of work in this field. In brief, the main advantages of EDXRD are that the X-ray high energies (*i.e.* 50–120 keV) present in the beam can penetrate and probe into large vessels. Furthermore, only minor modifications to create small entrance and exit windows on commercial autoclaves, which are standard equipment in many laboratories, are necessary in order to turn them into extreme-condition *in situ* reaction vessels. An additional advantage arises from the fact that there is no bias due to volume differences between the laboratory experiments and *in situ* reactions studied at the synchrotron (see Fig. 2.9.8).

The variety of scientific applications is huge: pressure-induced phase transitions of inorganic solids, hydrothermal synthesis of

microporous solids, intercalation, growth of layered perovskites and breathing in metal-organic frameworks, to name a few examples (see Walton & O'Hare, 2000). Extreme conditions can be reached in terms of temperature (~ 1273 K) in an autoclave with subsecond XRD time resolution. EDXRD in combination with large-volume autoclaves has provided otherwise-inaccessible information on many processes: intermediates in crystallization routes, activation energies for reactions, and kinetic parameters crucial for their understanding and optimization. The major disadvantage of EDXRD is that the resolution in the diffraction pattern is limited, since it is defined by the energy resolution of the solid-state detector. This effectively excludes all access to precise structural information. However, recent efforts have allowed quantitative phase analysis (Rowles, 2011; Rowles *et al.*, 2012). With the advent of third-generation synchrotrons, which provide orders of magnitude more flux at high energies, and the availability of high-energy flat-panel detectors, angular-dispersive diffraction data can successfully be collected from samples in large-volume cells. Their use expands the available information dramatically. To date, however, there are very few high-energy angular-dispersive beamlines, and the use of the large-volume cells in combination with EDXRD remains an active field and has recently been developed further by, for example, Moorhouse *et al.* (2012) at the Diamond Light Source. The cell there can be equipped with various reaction vessels made of alumina, steel, PTFE-lined steel or glassy carbon tubes depending on the chemical reaction to be studied. It can achieve temperatures as high as 1473 K with infrared lamps and has a magnetic stirrer to avoid sedimentation of the reaction products. In addition, Styles *et al.* (2012) have developed a large furnace and *in situ* cell for salt electrolysis.

Rijssenbeek *et al.* (2011) have studied a full-size battery cell with EDXRD (see Fig. 2.9.9). Diffraction data were collected during charge/discharge at high temperature of the sodium metal halide (Na/MCl_2 , $M = \text{Ni}$ and/or Fe) cells. They were able to assess the charge-state variations as a function of space and time in the cell during many charge/discharge cycles, and identify local crystal structures and phase distributions. The data confirm the propagation of a known well-defined chemical reaction front beginning at the ceramic separator and proceeding inward.

2.9.3.3.4. Large-volume cells for angular-dispersive diffraction

This application implies the use of monochromatic X-rays with extremely high energies (70 keV and above). Such energies can be easily reached on third-generation synchrotrons with in-vacuum undulators, thus providing sufficient flux for angular-dispersive diffraction experiments. The challenge with these experiments is to have a sufficiently high X-ray energy to penetrate large sample-cell vessels while maintaining reasonably good angular resolution in the diffraction pattern. When using large *in situ* cells with low-energy diffraction, there is a severe peak-broadening effect resulting in a deterioration of the data quality. At high energies, however, where the scattering angles are small, the sample thickness has little effect on the angular resolution provided that the area detector is positioned at a sufficient distance from the sample.

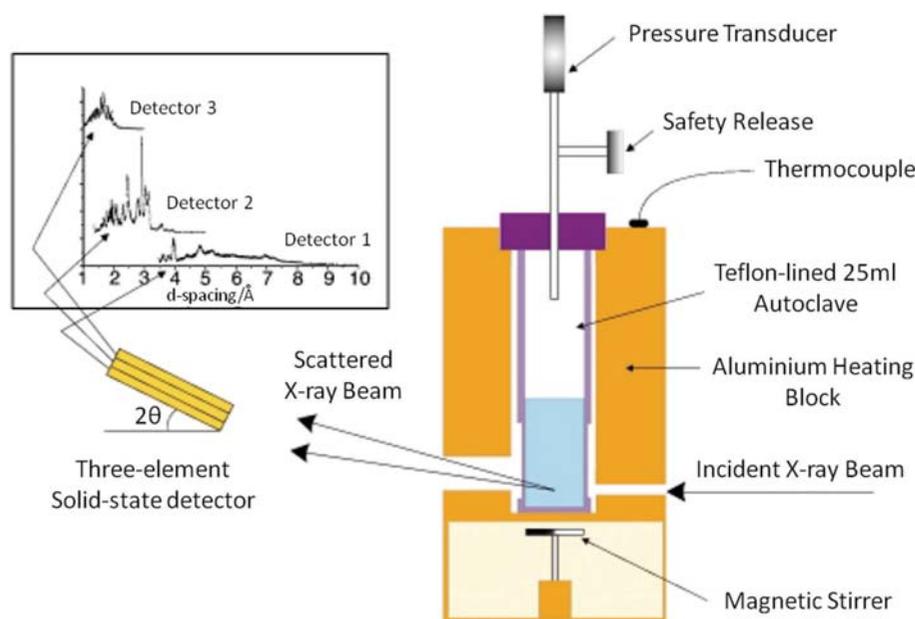


Figure 2.9.8

A schematic of the Oxford/Daresbury hydrothermal autoclave used for energy-dispersive X-ray diffraction studies. Adapted from Walton & O'Hare (2000) with permission of The Royal Society of Chemistry.

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O'Brien *et al.* (2011) explain the trade-offs for such experiments in detail and have shown that it is possible to extract useful structural information. Large-volume cells that used to be exclusively the domain of neutron diffraction and EDXRD have now also been adapted for angular-dispersive powder diffraction with, in some cases, increased speed and information content. For instance, Wragg *et al.* (2012) studied an industrial methanol-to-olefin conversion process with *operando* time- and space-resolved diffraction. The sample is rapidly scanned up and down to provide one-dimensional spatial information. The results complement earlier experiments performed with a microreactor. Jacques *et al.* (2011) extracted three-dimensional information by using dynamic X-ray diffraction computed tomography (XRD-CT). They measured over 50 000 diffraction patterns on beamline ID15 at the ESRF with different sample orientations, positions and temperatures. From this huge amount of data, they reconstructed the catalyst body in three dimensions with a diffraction pattern assigned to each volume unit within the sample as a function of time. With this information, they were able to follow the evolution of the catalytically active phase throughout the sample. Wragg *et al.* (2015) have since performed Rietveld analysis on voxels from the XRD-CT data for a methanol-to-olefin reactor bed. It is also worth mentioning work by Jensen *et al.* (2007), performed on beamline 1-ID at APS Argonne National Laboratory, investigating the kinetics of nanoparticle formation involving a sol-gel reaction in supercritical CO₂ at 10 MPa. The reaction was studied with XRD and small-angle X-ray scattering (SAXS) in a large 30 ml vessel. In a different application, Friščić *et al.* (2013) mounted a laboratory-scale 10 ml ball mill on the ID15 beamline in order to study mechanochemical reactions, which are used in numerous industrial production processes. By averaging ten 400 ms frames, they obtained sufficiently good data to perform full-pattern refinements and kinetic analysis, providing information about otherwise completely inaccessible processes. We therefore foresee a bright future for such extreme high-energy applications together

with large-volume studies, since they provide a useful bridge between the academic and industrial worlds.

2.9.3.4. Cells specifically for neutrons

2.9.3.4.1. Introduction

The special characteristics of neutrons imply both advantages and challenges for the design of *in situ* experiments and their associated equipment. The differences in penetration depths between X-rays and neutrons and the correspondingly smaller scattering cross sections for neutrons, together with the much lower flux densities, imply that cells for neutrons are quite different from the miniature capillary cells for X-rays described in the previous sections. Above all, the sample volume is by necessity often much larger than the equivalent volume required for a laboratory X-ray or synchrotron experiment. However, the ability of neutrons to penetrate deep into sample environments has been of great importance for studying samples at very low temperature, under high pressure or within strong magnetic fields. Similarly, reaction cells for *in situ* investigations profit from the ability of neutrons to penetrate through thick-walled vessels, for example for studying gas–solid reactions under high pressure. Only relatively recently, with the availability of high-energy synchrotron beamlines (>100 keV), can X-rays effectively compete with neutrons in this domain. Even in these cases, the very different scattering properties of neutrons (*e.g.* the strong variation of cross section with isotope) means that some measurements that are challenging, if not impossible, with X-rays can become quite feasible with neutrons. The solid–gas reaction of intermetallic phases with H₂ gas is a good example, where the positions of the interstitial H atoms can be located within a heavy-metal hydride (Kamazawa *et al.*, 2013). Similarly, the hydration of cement has been investigated many times, with improved time resolution resulting from developments in neutron optics and detector performance. *In situ* studies of oxidation reactions have also benefited from the better ability of

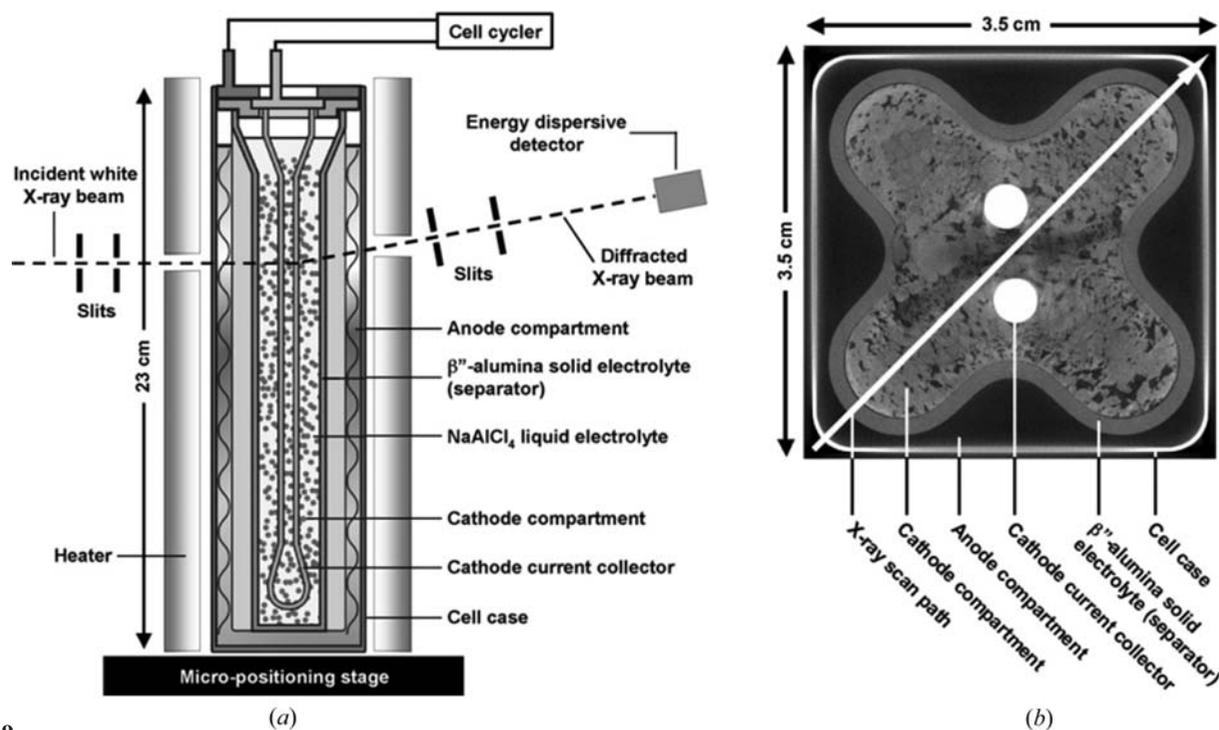


Figure 2.9

(a) Schematic of a sodium-halide cell in an *in situ* synchrotron EDXRD experimental setup. (b) Cross-sectional computed tomography image of a cell. The arrow along the cell diagonal denotes the path of the X-ray line scans used in this work. This corresponds to an X-ray penetration depth of up to 50 mm. Adapted from Rijssenbeek *et al.* (2011) with permission from Elsevier.

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neutrons to determine the atomic positions of oxygen during synthesis (Bianchini *et al.*, 2013). The investigation of chemical processes in the electrodes of batteries has, for example, been particularly fruitful. Once again, specialist cells for electrochemistry have been developed that take advantage of the penetration power of the neutrons in order to reveal bulk behaviour within the electrode material. Examples of these and other applications are given in an extensive review of *in situ* and time-resolved neutron scattering (Isnard, 2007) and in the more recent articles by Hansen & Kohlmann (2014), Sharma *et al.* (2015) and Pang & Peterson (2015). It should also be noted that different geometrical arrangements are used in angular-dispersive monochromatic neutron diffraction or when using a fixed-angle detector bank for time-of-flight neutron diffraction, which can have important implications for the cell design. In the following sections, we will examine some of these specialist cells in more detail.

2.9.3.4.2. Solid-gas reactions

Suitable storage media for hydrogen and other small molecules include hydrides, hydrates, clathrates and other microporous materials [*e.g.* metal-organic frameworks (MOFs)]. *In situ* neutron powder diffraction has been the method of choice to investigate solid-gas reactions involving light molecules reacting with these types of framework structures, and a wide variety of *in situ* cells have been developed for this purpose. The design of the cell can be quite primitive, yet still be very successful for this kind of application. As a simple example, we consider the study of the reduction of a perovskite-related oxide under flowing hydrogen carried out at D20 at the Institut Laue-Langevin (ILL) in Grenoble (Tonus *et al.*, 2009). The powder sample was loaded into a quartz tube (12 mm diameter) and mounted in the standard D20 furnace. The tube was connected to a flow of reducing gas controlled by a needle valve. High-quality data could be collected in a short time (a few minutes) at high temperature under flowing H₂ gas, in this case up to a maximum temperature of 973 K. Occupancy factors for the different oxygen sites could be refined as a function of temperature under reducing and oxidizing conditions.

In another example, the goal was to investigate solid-gas reactions under pressures of 16 MPa and temperatures up to 673 K (Widenmeyer *et al.*, 2013). Since the use of thin-walled single-crystal sapphire capillaries has become routine in synchrotron powder X-ray diffraction, the authors decided to adopt a similar strategy for the neutron-diffraction experiment. In this case, they selected a 6 mm diameter sapphire tube with steel end caps and metal seals. Pressures of 16 MPa could be achieved over periods of days without measurable pressure loss, and the powder data were of high quality, allowing Rietveld refinement of crystal structures including light-atom positions, displacement parameters and site occupancies. In addition to providing good-quality data and a low background, the sapphire tube also has the advantage of being chemically very robust and hence avoiding, for example, the problem of hydrogen embrittlement.

2.9.3.4.3. Electrochemistry using neutron diffraction

The advantages of high penetration and sensitivity to light elements such as hydrogen, oxygen and lithium make neutron powder diffraction an interesting tool for investigating processes occurring within complex electrochemical systems. Lithium-ion batteries are one of the most widely used portable energy

sources. These devices rely on the insertion of lithium ions into both positive and negative electrodes. A proper understanding of the structural processes that occur at the electrodes can only be obtained from *in situ* diffraction experiments performed during electrochemical charging and discharging. A suitable electrochemical cell for this type of measurement has been reported by Rosciano *et al.* (2008). The challenge for the design of this type of cell is to enable the neutron-diffraction data to be collected with the minimum of hindrance, while allowing electrochemical characterization to be performed at the same time. In addition, the fact that most separators and polycarbonate-based electrolyte solutions contain large amounts of hydrogen presents problems due to the large incoherent neutron-scattering cross section of hydrogen, which results in a deterioration in the signal-to-background ratio. However, as pointed out by Sharma *et al.* (2011), designs have been developed that minimize the amount of electrolyte required, and, where possible, deuterated solution can be used. Using a home-made design of a rollover, cylindrical cell that mimicked the geometry of commercial batteries, Sharma *et al.* (2011) were able to probe structural changes in real time (5 min per pattern) as a function of electrochemical cycling using the Wombat powder diffractometer (ANSTO). Sharma *et al.* (2015) have since reviewed both synchrotron and neutron electrochemistry cells. Pang & Peterson (2015) provide an overview of all lithium-ion and sodium-ion battery materials studied by neutron powder diffraction *in situ* since 1998.

Battery materials and fuel cells are extensively used in a vast variety of applications in energy conversion and storage, and there is no doubt that *in situ* neutron powder diffraction will continue to play an important role in the efforts to further improve the performance of these materials. In Japan, for example, a new neutron-diffraction instrument (SPICA at the J-PARC spallation source) will be used to analyse atomic structures and the behaviour of batteries during their charge cycle. Both at spallation and reactor-based neutron sources, improvements in neutron optics and detector performance have reduced both the volume of sample needed for *in situ* experiments and the time required to collect each powder pattern.

2.9.3.4.4. Hydrothermal reaction cells

Many materials with potential applications in technologically important fields can only be prepared by the supercritical hydrothermal synthesis method. A detailed knowledge of the reaction mechanisms is lacking, mainly because the processes take place within sealed and thick-walled reaction vessels. A technique is required that can penetrate the walls of the vessel during the reaction, and can reveal the kinetics and mechanism of bulk sample synthesis. Neutron diffraction is the ideal tool for this task. For example, Ok *et al.* (2010) constructed a relatively simple chemical-reaction cell for investigating syntheses, even under extreme supercritical conditions, using of time-of-flight techniques. The cell itself was machined from a single ingot of Inconel, and had a maximum wall thickness of 4.0 mm. Thinner sections of 2.7 mm thickness were used in parts of the cell to reduce attenuation of the incident and scattered neutron beams. The vessel had a normal working pressure and temperature of 40 MPa at 723 K. The experiments were carried out on the POLARIS diffractometer at the ISIS pulsed spallation neutron source.

Another example of a hydrothermal reaction cell of somewhat different design is that used by Xia *et al.* (2010). In this case, a large sample volume was chosen (320 ml internal volume) to

allow bulk properties to be investigated. The cell had a dumbbell configuration, assembled from commercial stainless-steel components, that held most of the hydrothermal liquid, and a zero-scattering Ti–Zr alloy sample compartment with a 0.4 mm wall thickness. This choice of material and wall thickness for the sample cell dramatically reduced the background scattering from the container, but limited the operational range to temperatures up to 573 K and pressures up to 9 MPa. The cell was commissioned at the Wombat neutron powder diffractometer at ANSTO, using the *in situ* kinetic study of the hydrothermal phase transformations from leucite (KAlSi₂O₄) to analcime (NaAlSi₂O₆·H₂O) as a demonstration of the capabilities of the equipment.

2.9.4. Complementary methods and future developments

Standard crystallographic powder-diffraction methods can provide information about component phases and particle size, and can also be used to determine crystal structure, but the data quality required means that long-range crystalline order needs to be present. However, many real systems have amorphous components or demonstrate various degrees of disorder. In order to provide complementary information on the disordered components, alternative techniques are needed. In the early 1990s, Couves and co-workers started to combine XRD with XAFS in one setup in order to complement the XRD data (Couves *et al.*, 1991); they were quickly followed by Clausen and co-workers (Clausen *et al.*, 1993). Shortly afterwards, small-angle scattering (Dokter *et al.*, 1994) and vibrational spectroscopic techniques such as infrared and Raman were also added to complement the diffraction information (Newton & van Beek, 2010). More recently, a very old technique (Tarasov & Warren, 1936) based on the pair distribution function (PDF) has become immensely popular with the advent of high X-ray energies and efficient detectors (Chupas *et al.*, 2003). The PDF technique does not depend upon any assumptions about long-range crystalline order and can therefore be used to extract information on amorphous materials, defect structures and the structures of nanoparticles (see Chapter 5.7). It has the same huge variety of applications as traditional diffraction methods, and provides complementary information. Several of the *in situ* cells described above can also be used for combined techniques and PDF experiments at synchrotrons. One of the many reasons behind the rapid success of the PDF method is the availability of well developed software for data analysis (Juhás *et al.*, 2013) and modelling (Neder & Proffen, 2008).

We have seen in some of the examples above that acquisition times are reaching down into the millisecond range and the quantity of data being delivered by modern systems is becoming increasingly difficult to analyse. There is progress in automated sequential and parallel parametric refinements with traditional data-analysis software. However, we believe new strategies are necessary in order to make better, more efficient use of modern detectors. There are efforts in this direction in automated chemometric methods (Burley *et al.*, 2011) stemming from spectroscopy. However, these algorithms are not always well adapted to analyse data derived from powder-diffraction measurements. Chernyshov *et al.* (2011) have performed theoretical and experimental work taking the interference nature of diffraction into account in their method, which is based on modulation. Nevertheless, improvements in data analysis are still trailing far behind experimental progress and much effort will be necessary in this area. Choe *et al.* (2015) have even performed

stroboscopic high-resolution powder diffraction on piezoelectric ceramics, detecting sub-millidegree shifts with microsecond time resolution.

In contrast to the pursuit of speed, the Diamond Light Source have decided to extend their powder-diffraction beamline and make it suitable for experiments lasting several months or even more, by moving slowly aging samples automatically into the measurement position at regular intervals (hours, days or even weeks) in a long-duration experiment (LDE) facility. Relevant applications are in batteries, fuel cells, crystallization, gas storage, mineral evolution, seasonal effects, thermal and electrical power cycling, and corrosion science.

In addition to the developments in instrumentation presented here, the availability of new radiation sources is opening up many interesting possibilities for studying chemical reactions. Not only are more, and better equipped, synchrotron beamlines becoming operational, but there are new facilities in planning or under construction that will dramatically change the way in which chemical processes can be investigated. New spallation sources and free-electron lasers (FELs) open up new possibilities in the time and space domains. In particular, FELs will facilitate the study of reactions on sub-picosecond timescales. Preliminary experiments using picosecond to nanosecond time resolution have already been carried out on synchrotron beamlines to investigate transient structural changes in organic powders (Techert *et al.*, 2001). It is evident that the huge increase in flux per pulse and the much shorter pulse length available from FELs will open up completely new dimensions in the field of *in situ* experiments.

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