

2.9. IN SITU CHEMICAL-REACTION CELLS

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

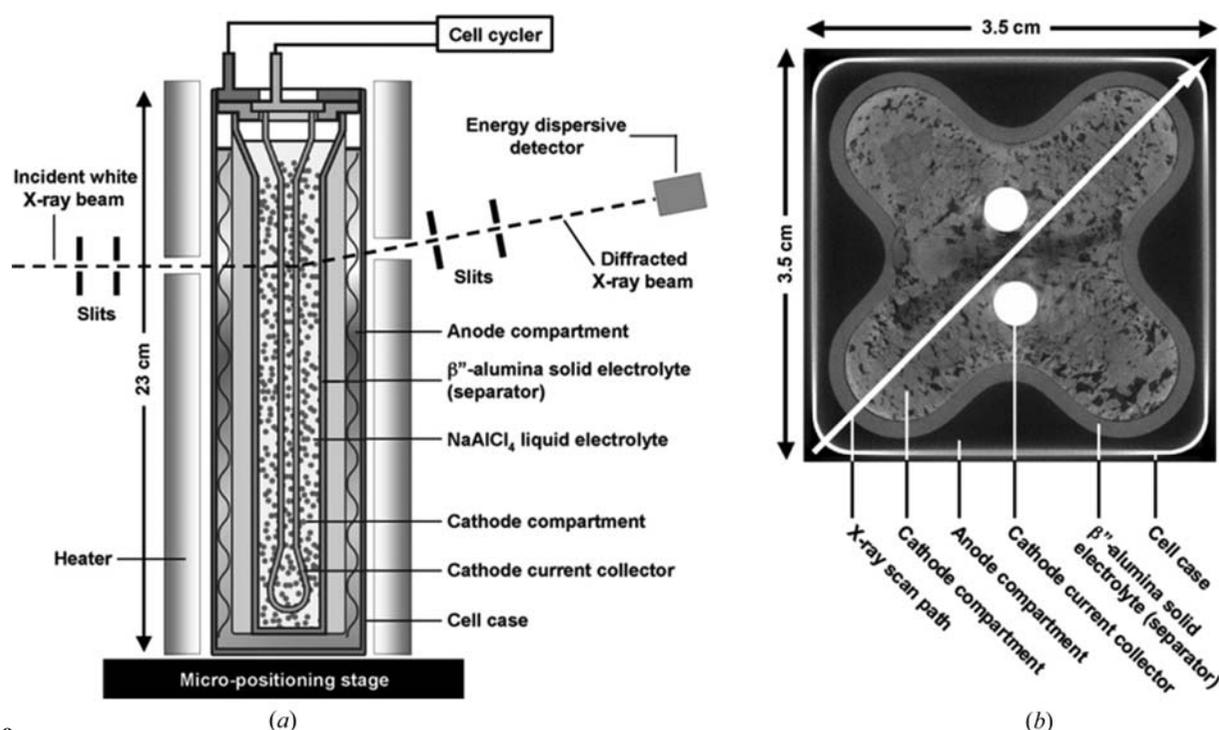


Figure 2.9.9

(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.

2. INSTRUMENTATION AND SAMPLE PREPARATION

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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