

2.9. IN SITU CHEMICAL-REACTION CELLS

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

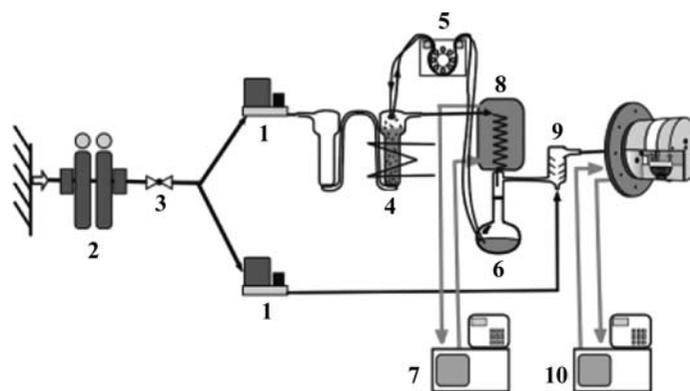


Figure 2.9.6

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

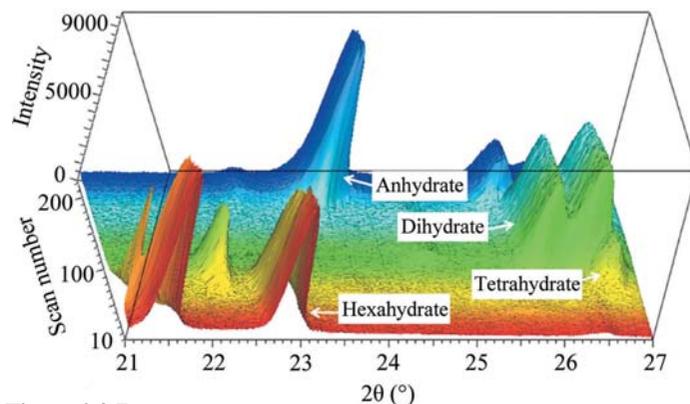


Figure 2.9.7

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.

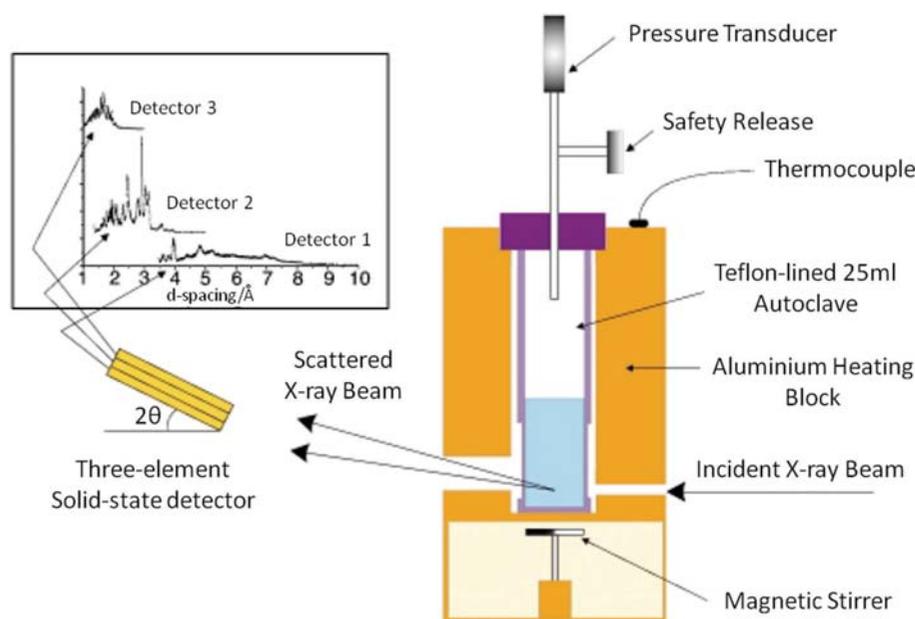


Figure 2.9.8

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.