

2. INSTRUMENTATION AND SAMPLE PREPARATION

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

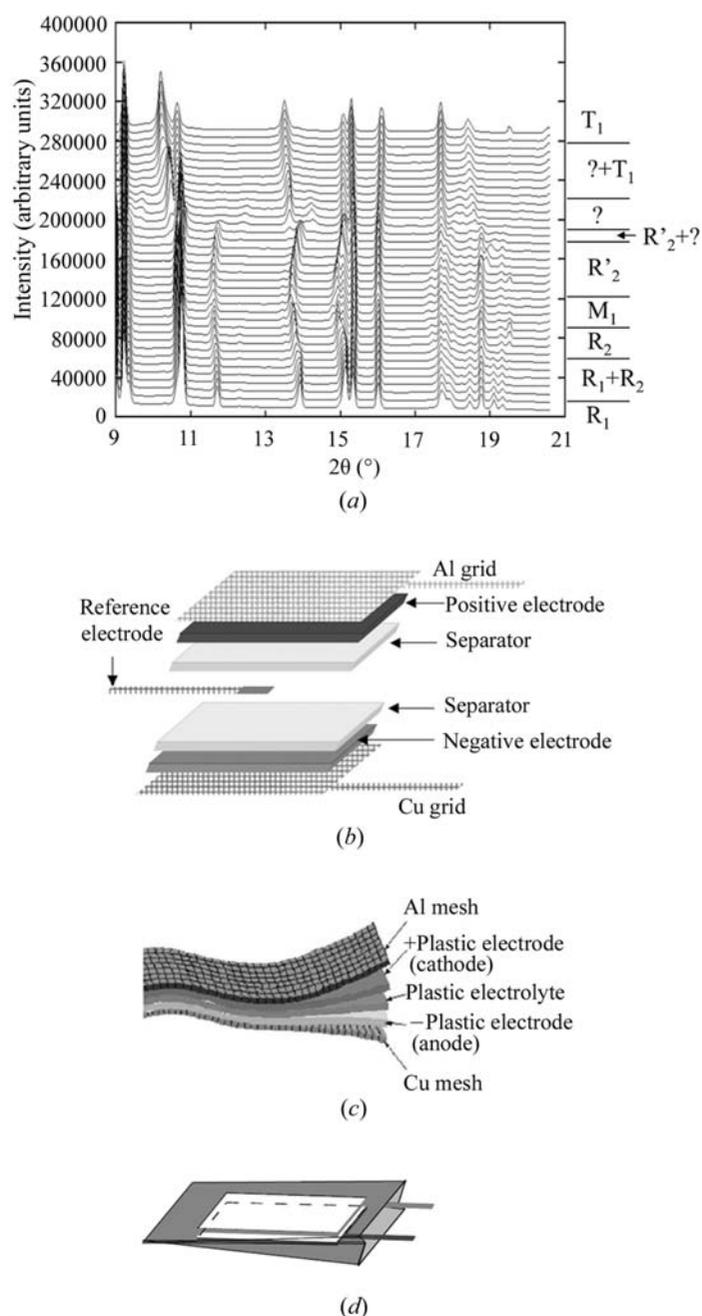


Figure 2.9.5

(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.

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

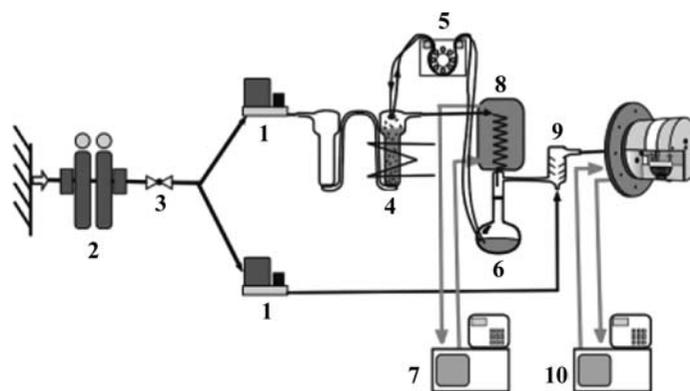


Figure 2.9.6

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

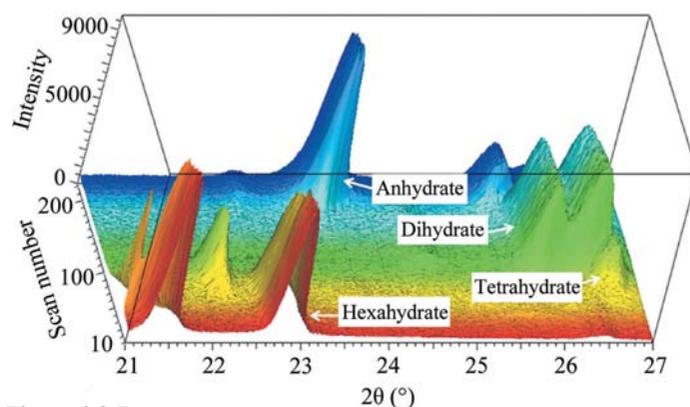


Figure 2.9.7

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).