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 electro-chemical 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 electro-chemistry 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
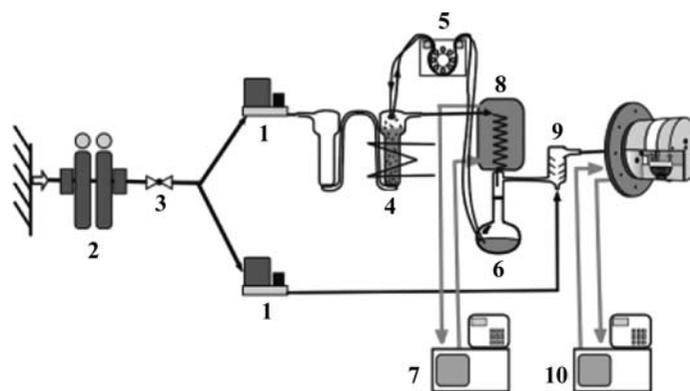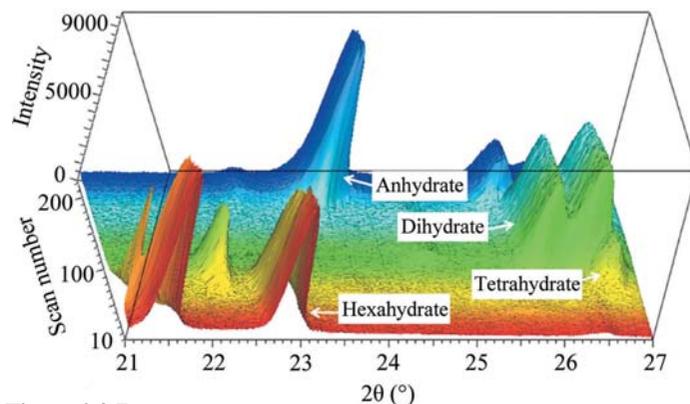

Figure 2.9.6
Schematic drawing of the humidity-control system: (1) mass-flow controller, (2) adsorption dryer, (3) pressure regulator, (4) heated bubbler, (5) peristaltic pump, (6) water reservoir, (7) thermostat, (8) condensation trap, (9) mixing chamber and (10) thermostat. Adapted with permission 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, $Mg(ClO_4)_2 \cdot nH_2O$, 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).

references