

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

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### 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.

## 2. INSTRUMENTATION AND SAMPLE PREPARATION

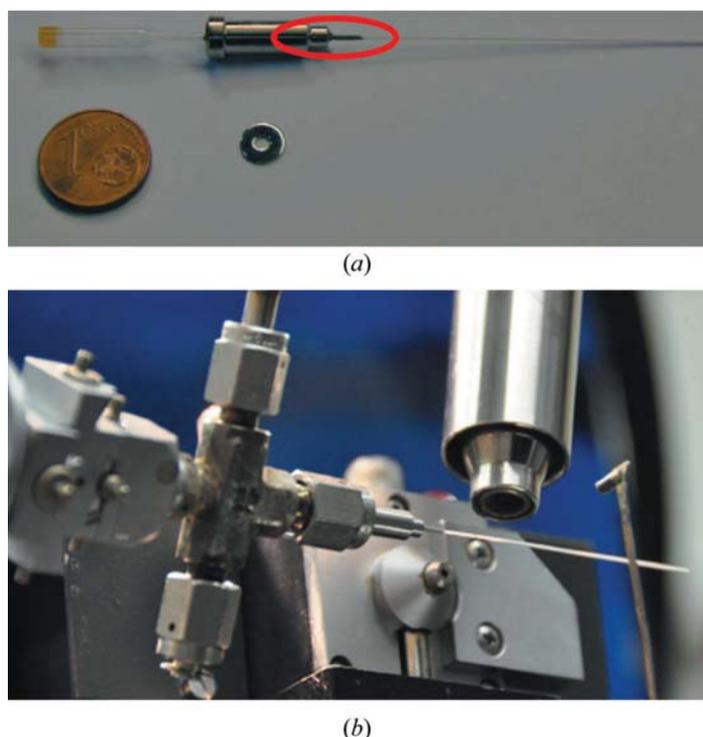
### 2.9.3.2. Capillary cells

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

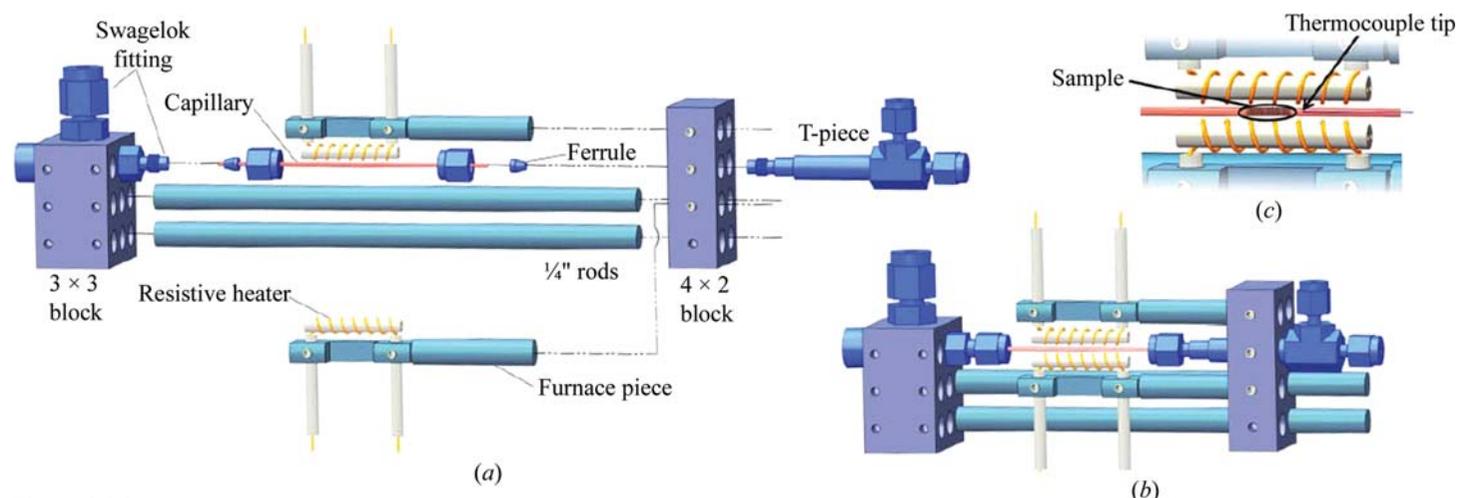
temperatures ranging from 80 to 1000 K with cryogenic and hot-air blowers or resistive heaters close to the sample. Static gas pressures can be as high as 30 MPa and in flow cells 2 MPa is commonly reached, as well as vacuum conditions. Capillary cells were first applied by Clausen (1991) and have been 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.

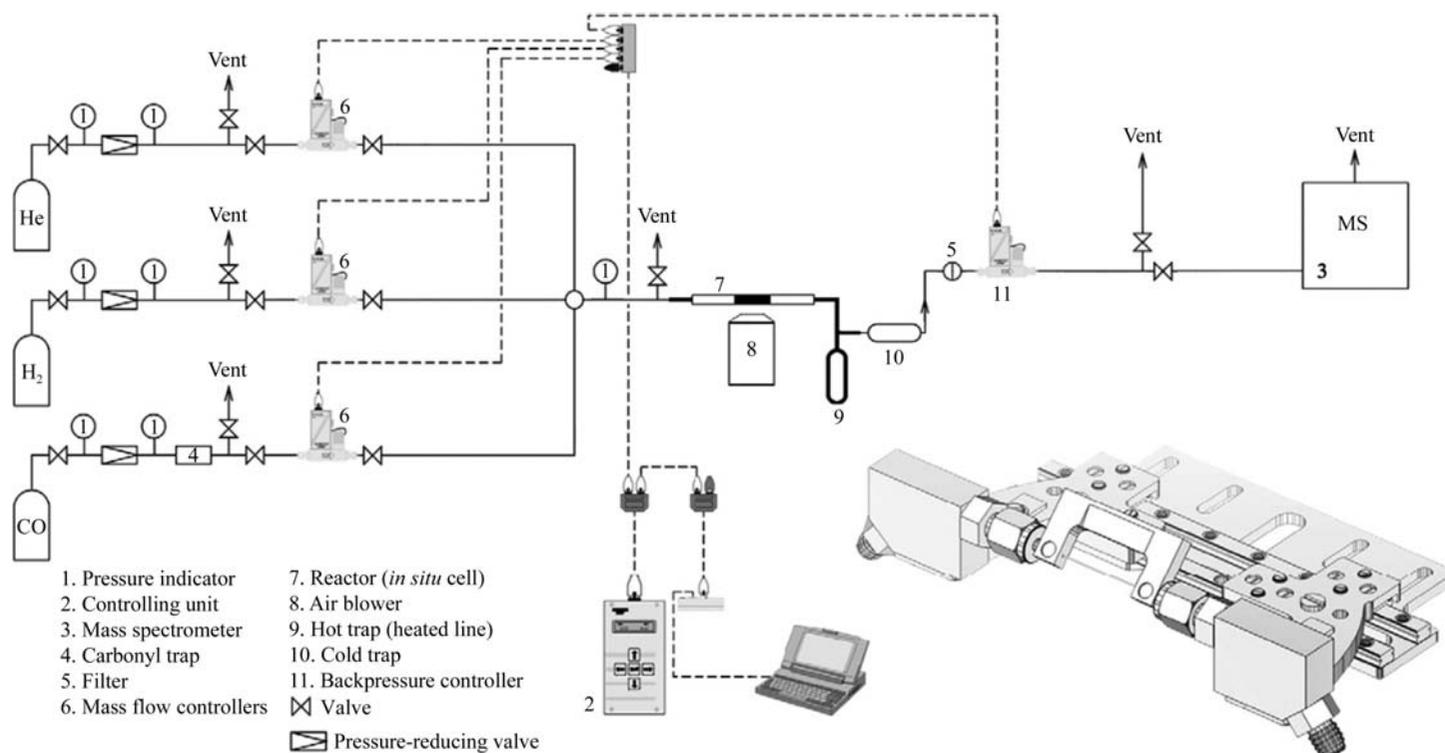


**Figure 2.9.1**  
(a) Swagelok VCR gland with an epoxy-glued capillary (red ellipse). (b) VCR capillary cell on a beamline with a cryostream (adapted from Jensen *et al.*, 2010).



**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).

## 2.9. IN SITU CHEMICAL-REACTION CELLS

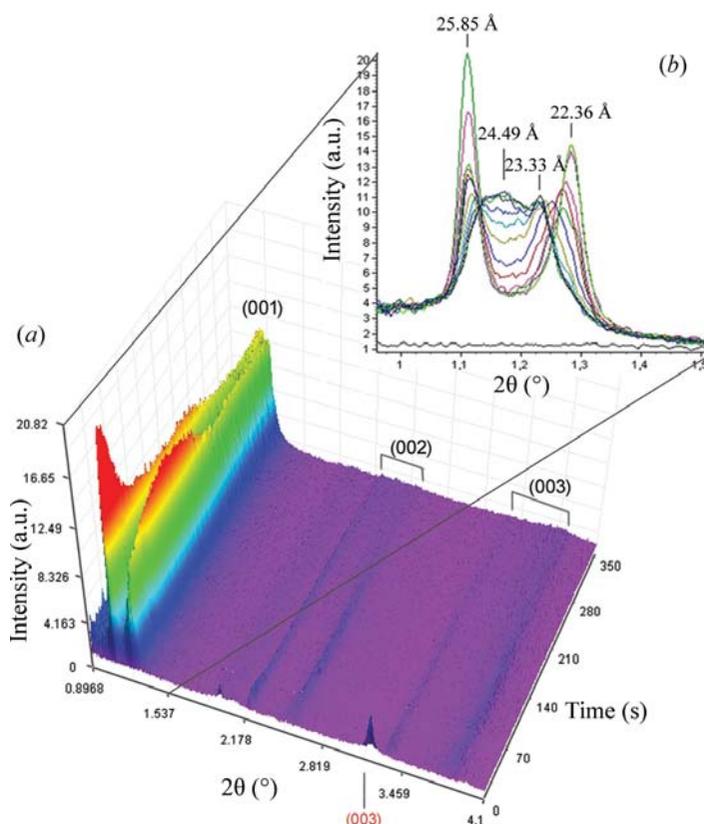


**Figure 2.9.3**

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  $\sim 4$  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.

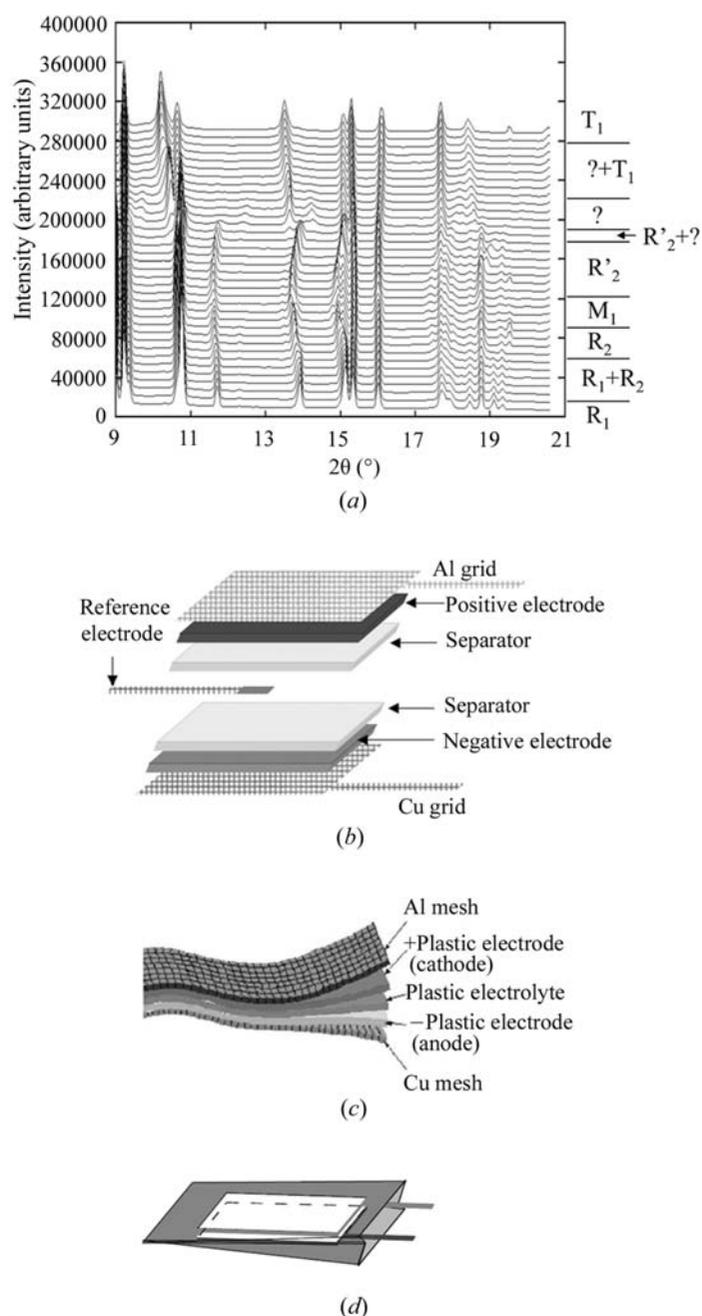
If the miniaturization turns out to be problematic, one could consider measuring bulky ( $\sim 1$  cm or more) samples and/or using larger reaction vessels in combination with either energy-dispersive diffraction or extremely high X-ray energies (Tschentscher & Suortti, 1998). This gives the additional 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  $\text{LiCoO}_2/\text{Li}$  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.