

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

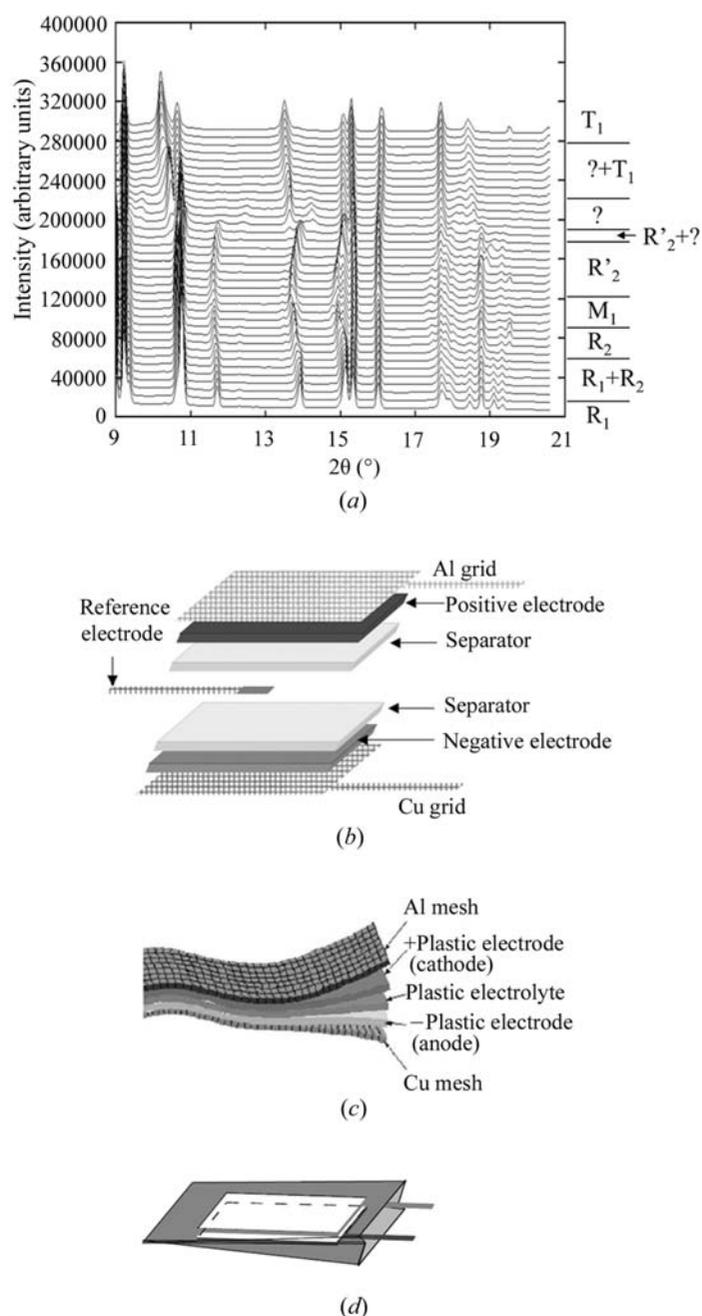


Figure 2.9.5

(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.