

2. INSTRUMENTATION AND SAMPLE PREPARATION

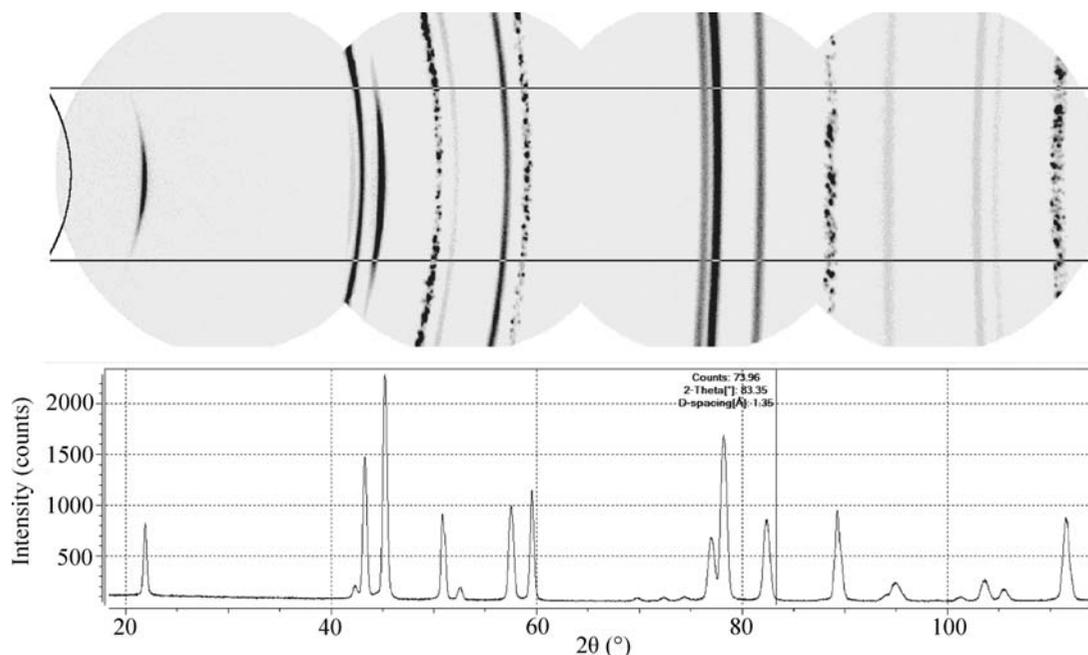


Figure 2.5.16
Diffraction pattern merged from four 2D frames collected from a battery material.

sequential 2θ ranges can be collected. The integrated profiles can then be merged to achieve a large 2θ range. Fig. 2.5.16 shows four 2D frames collected from a battery material with a microgap detector. The slice integration region is defined by two conic lines and two horizontal lines. The diffraction profile integrated from the merged frames is displayed below.

2.5.4.1.3. Defocusing effect

A 2D diffraction pattern over a range of 2θ is measured simultaneously with a single incident angle, so the incident angle has to be lower than the minimum 2θ angle. Since the reflected angle cannot always be the same as the incident angle, geometric aberrations are observed. The defocusing effect occurs when the incident angle is lower than the reflection angle. At low incident angles, the incident beam spreads over the sample surface into an area much larger than the size of the original X-ray beam. The observed diffracted beam size is magnified by the defocusing effect if the diffracted beam makes an angle larger than the incident angle. The defocusing effect for reflection-mode diffraction can be expressed as

$$\frac{B}{b} = \frac{\sin \theta_2}{\sin \theta_1} = \frac{\sin(2\theta - \omega)}{\sin \omega}, \quad (2.5.46)$$

where θ_1 is the incident angle, b is the incident beam size and B is diffracted beam size. The ratio of B to b is a measurement of the geometric aberration and will be referred to as the defocusing factor. In principle, defocusing occurs only when B/b is larger than 1. The reflected beam is actually focused to the detector when $\theta_2 < \theta_1$. The defocusing effect occurs when $\theta_2 > \theta_1$ and the defocusing factor increases with increasing θ_2 or decreasing θ_1 . The maximum defocusing appears at $\theta_2 = 90^\circ$. For the θ - 2θ configuration, the incident angle $\omega (= \theta_1)$ is used in the equation.

For B-B geometry with a divergent slit and receiving slit of the same size the defocusing factor is always 1. With a 2D detector the defocusing factor varies with the 2θ angle. If a large 2θ range is measured on a flat sample in reflection mode, it is always desirable to collect several frames at different incident angles for each 2θ range so as to improve the 2θ resolution. A cylindrical

detector may collect a diffraction pattern over a large 2θ range (Gelfi *et al.*, 2005). However, the defocusing effect prevents it from being used for a large 2θ range for a flat sample. Fig. 2.5.17 compares the effect for a flat detector and a cylindrical detector. Fig. 2.5.17(a) shows a cylindrical detector being used to collect a diffraction pattern from a flat sample for a 2θ range of 5 to 80° . The incident angle must be kept at 5° or lower. Fig. 2.5.17(b) shows a flat detector being used to collect the diffraction pattern over the same 2θ range. In order to minimize the defocusing effect, the data collection is done at four different incident angles (5° , 15° , 25° and 35°) with four corresponding detector swing angles (10° , 30° , 50° and 70°). Fig. 2.5.17(c) compares the defocusing factors of the two configurations. The horizontal dot-dashed line with defocusing factor $B/b = 1$ represents the situation with B-B geometry. The defocusing factor continues to increase with 2θ angle up to $B/b = 11$ for cylindrical detector. That means that the 2θ resolution would be 10 times worse than for the B-B geometry. For the diffraction pattern collected with a flat detector in four steps, the defocusing factor fluctuates above 1, with the worst value being less than 3. Another approach to avoiding defocusing is to collect the diffraction pattern in transmission mode. There is no defocusing effect in transmission when the incident beam is perpendicular to the sample surface. Therefore, the transmission pattern has significantly better 2θ resolution. Transmission-mode diffraction also has other advantages. For instance, the air scattering from the primary beam may be blocked by a flat sample, therefore lowering the background from air scattering. However, transmission-mode diffraction data can only be collected from samples with limited thickness, and the maximum scattering intensity is achieved at low 2θ angles with a sample thickness of $t = 1/\mu$, where μ is the linear absorption coefficient. The scattering intensity drops dramatically when the thickness increases.

2.5.4.1.4. Sampling statistics

In powder X-ray diffraction, the number of crystallites contributing to each reflection must be sufficiently large to generate reproducible integrated peak intensities (see Chapter 2.10). A larger number of contributing crystallites gives better precision or sampling statistics (also referred to as particle