

Microstructural characterisation of battery materials using powder diffraction data: DIFFaX, FAULTS and SH-FullProf approaches

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Abstract

The microstructure of Li_2PtO_3 , isostructural with Li_2MnO_3 , and $\beta\text{-Ni}(\text{OH})_2$ is analyzed from powder diffraction data using two approaches. Firstly, the recently developed FAULTS program (a modification of the DIFFaX program to allow refinement of the diffraction pattern) is used to include different amounts and types of stacking faults in the microstructural description of the material. This approach treats size effects mostly isotropically and assigns most of the anisotropic peak broadening to stacking faults. On the other hand, the FullProf program is also used to perform Rietveld refinement with microstructural models that treat the effects of anisotropic size and hence considers that this is the main contribution to broadening. The simultaneous use of these two approaches allows choosing the most adequate model in each particular case in order to obtain an accurate description of the microstructure of the material.

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1. Introduction

Polycrystalline materials invariably contain imperfections that can deeply influence their physical, mechanical and chemical properties, and battery materials are not an exception to this rule. The microstructural characterisation of these materials is of essential importance as it may have an important effect upon the electrochemical properties. Powder diffraction is now one of the most widely used techniques available to materials scientists for studying the structure and microstructure of crystalline solids. Microstructural features can strongly modify diffraction line profiles, leading to broadened and occasionally shifted or asymmetric diffraction lines. These features include finite crystallite size, extended defects such as stacking faults and the existence of microstrains that induce fluctuations in cell parameters. Unfortunately, correlation between the diffraction line profile and microstructural features is not direct and, moreover, superposition of different phenomena is common which turns the microstructural characterisation of solids into a complex task.

So far, a widely used tool to interpret the diffraction data of one-dimensionally disordered systems is the DIFFaX program, [1] which allows the simulation of powder X-ray and neutron diffraction patterns of defective materials. However, simulation leads only to qualitative results. To overcome this issue we have developed the new FAULTS program, [2] a code based on DIFFaX that allows not only simulation but also refinement of the experimental pattern, thus yielding much more accurate results. Another commonly used tool for the structural characterisation of matter is the Rietveld method, also based in diffraction patterns refinement, which can include specific microstructural models.

In this paper, we present two case examples of materials with different microstructural characteristics that have been studied by using both approaches: FAULTS and Rietveld refinement. For the latter we have used the FullProf program [3] that can model anisotropic size broadening with linear combinations of spherical harmonics (SH) [4]. While the FAULTS program assigns anisotropic line broadening to stacking faults and simulates size effects mainly isotropically, the SH approach reproduces anisotropic size broadening but cannot model the broadening caused by stacking faults. These assumptions have to be kept in mind when analyzing microstructural features.

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The first example is Li_2PtO_3 which has been studied as cathode material for lithium batteries and has been reported to have a volumetric capacity comparable to LiCoO_2 [4]. This compound is isostructural with Li_2MnO_3 and Li_2PdO_3 and it is also constituted of alternate Li and Li/Pt layers with oxygen in between. Similarly to Li_2MnO_3 [5], the XRD pattern of this material exhibits some reflections at low angles that are indicative of a honeycomb ordering of the lithium/transition metal layers and the Warren shape of the diffraction peaks certainly indicates the presence of stacking faults within the structure.

The second example is $\beta\text{-Ni(OH)}_2$, used as the positive electrode material in nickel batteries for more than a century, for which it is now generally accepted that lack of perfection in crystallization must be taken as a sine qua non reason for electroactivity. The X-ray diffraction patterns of the electroactive materials present anisotropic abnormal peak broadening that was commonly considered to be originated by stacking faults [6]. In agreement with this, previous works in DIFFaX simulations [7,8] showed that certain amounts of stacking faults could result in anisotropic peak broadening.

2. Experimental

Li_2PtO_3 was prepared according to the method described in reference [4] and was always contaminated by small amounts of Pt. The X-ray powder diffraction pattern of this compound was recorded with a SiemensD-501 with $\text{Cu K}\alpha_1 = 1.5406 \text{ \AA}$, $\text{Cu K}\alpha_2 = 1.5444 \text{ \AA}$ radiation in the range $2\theta = 14\text{--}124^\circ$ at a 0.02° scanning step. The instrumental resolution function (IRF) was obtained from a well crystallized La_2CrO_6 sample.

For the $\beta\text{-Ni(OH)}_2$ case, two samples with different microstructural characteristics were prepared. Sample S1 was obtained by addition of nickel nitrate 1 M to 28% NH_4OH at 60°C in potassium hydroxide 5 M [9] and sample S2 was synthesized by direct precipitation of $\beta\text{-Ni(OH)}_2$ from a 1 M solution of nickel sulphate with 2 M sodium hydroxide at 70°C [8]. This later method is widely used in the industrial preparation of electroactive $\beta\text{-Ni(OH)}_2$. Finally, an industrial commercial sample was also studied (sample I) that contains cobalt as a doping element. Its chemical composition was found to correspond to $\text{Ni}_{1-x}\text{Co}_x(\text{OH})_2$ ($x = 0.012$). $\beta\text{-Ni(OH)}_2$ X-ray diffraction patterns were collected using a Siemens D-500 diffractometer with $\text{Cu K}\alpha_1 = 1.5406 \text{ \AA}$, $\text{Cu K}\alpha_2 = 1.5444 \text{ \AA}$ radiation in the range $2\theta = 5\text{--}105^\circ$ at a 0.03° scanning step. The samples were side loaded in order to minimize texture effects and the IRF was obtained from a LaB_6 standard material.

The FAULTS program, as DIFFaX, needs an input file where the defective structure has to be described in terms of a stacking sequence of layers of atoms. Each type of layer can interconnect with the others via stacking operations that occur with a certain probability. In order to describe the defective layered structure, it is necessary to define the unit cell, the atomic positions in each layer type and the stacking/transition vectors. In the $\beta\text{-Ni(OH)}_2$ case, size effects were also taken into account as FAULTS allows the refinement of the size parameters that correspond to the Gaussian (D_g) and Lorentzian (D_l) contributions to the full width at half maximum (FWHM) [10]. In order to include a certain degree of size anisotropy, as $\beta\text{-Ni(OH)}_2$ samples exhibit a platelet-like morphology, the number of layers per crystallite was also considered. The quality of the agreement between observed and calculated profiles is given by the conventional R_p value [11].

Rietveld refinements were carried out with the FullProf program (Windows version, April 2004) using the pseudo-Voigt profile function of Thompson et al. [12]. To treat anisotropic size effects the Lorentzian part of the peak broadening was modeled with linear combinations of spherical harmonics (SH) which allow the calculation of the crystallite average size along each reciprocal lattice vector. An average apparent shape of the crystallites can also be displayed using the GFOURIER 04.02 program [13].

3. Results and discussion

3.1. Microstructural analysis of Li_2PtO_3

The powder X-ray diffraction pattern recorded is in full agreement with that described in reference [4]. Li_2PtO_3 is isostructural with Li_2MnO_3 [5] and Li_2PdO_3 [14], and can be indexed with the $C2/m$ space group. The superstructure peaks in the range $2\theta = 17\text{--}32^\circ$ indicate that the Li/Pt atoms of the mixed layer are arranged following a “honeycomb” ordering scheme (see Fig. 1).

Rietveld refinement of Li_2PtO_3 using the FullProf program and the $C2/m$ space group leads to refined cell parameters with values $a = 5.190(4) \text{ \AA}$, $b = 8.983(2) \text{ \AA}$ and $c = 5.112(3) \text{ \AA}$, and $\beta = 109.9(1)^\circ$. However, as it is shown in Fig. 2, Rietveld refinement is unable to model the Bragg intensities and the Warren fall that appears in the $2\theta = 20\text{--}35^\circ$ angular range (shown in the inset of Fig. 2), which indicates, as for Li_2MnO_3 , a certain degree of short range disorder that may be due to defects in the stacking arrangement of the honeycomb layers. For the refinement of stacking faults the FAULTS program was used. Fig. 3 shows two

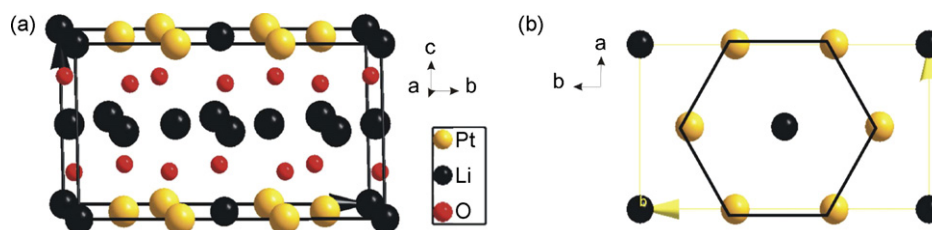


Fig. 1. (a) Li_2PtO_3 $C2/m$ unit cell and (b) view of the Li/Pt layers where the honeycomb arrangement can be observed.

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