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Anisotropic „X-ray diffraction“ dimensions of ellipsoid-shaped crystallites of cathode powders $LiFePO_4$

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The relationship between the anisotropic dimensions of powder crystallites obtained by X-ray diffraction ($D_{i\,\mathrm{XRD}}$), and their linear dimensions (L_i) has been investigated by numerical calculations. The following analytical expression is found for the orthorhombic lattice of ellipsoidal $LiFePO_4$ crystallites with their lognormal size distribution: $D_{i\,\mathrm{XRD}} = (3/4 + 0.38W_i^2)\bar{L}_i$, where $\bar{L}_i$ and W_i — the mean value of the size and the variance of this distribution along the i-th crystallographic axis. The use of the obtained expression allows increasing the accuracy of complementary X-ray and electron-microscopic measurements for the purpose of experimental determination of parameters of projections of the function of (marginal) distributions on axes and correlation coefficients between them.

Keywords: $LiFePO_4$, marginal size distribution, lognormal distribution.

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For a hypothetical powder of identical crystallites, the value of their „X-ray diffraction“ size (the size obtained using the X-ray diffraction method) D_{XRD} is equal to the volume-averaged column length of the crystallite [1,2]. For example, Fig. 1 shows an anisotropic crystallite and an M_1 column along the 1st crystallographic direction, whose averaging is described by equation

$$D_{1\,\mathrm{XRD}} = \bar{D}_1(M_1) = \frac{1}{V}\int M_1 dV = \frac{1}{V}\iint M_1^2 dx_2 dx_3 = \frac{3}{4}\bar{L}_1, \qquad (1)$$

where V — the volume of the crystallite. The last equality is valid for ellipsoidal crystallites with orthogonal axes [3,4]. Variations of non-orthogonal axes are described in [5] detail. This result for an ellipsoid can be obtained from its canonical equation

$$\frac{x_3^2}{\left(\frac{L_3}{2}\right)^2} + \frac{x_2^2}{\left(\frac{L_2}{2}\right)} + \frac{\left(\frac{M_1}{2}\right)^2}{\left(\frac{L_1}{2}\right)^2} = 1, \qquad (2)$$

in which $x_1 = \frac{M_1}{2}$. Hence, we obtain

$$M_1 = L_1\left(1 - \left((2x_2)/L_2\right)^2 - \left((2x_3)/L_3\right)^2\right)^{1/2}. \qquad (3)$$

In (1), the double integration is performed over the area Reg of the central section of the ellipsoid perpendicular to the 1st axis:

$$Reg = \left((2x_2)/L_2\right)^2 + \left((2x_3)/L_3\right)^2 \leqslant 1. \qquad (4)$$

For real samples, their size distribution must be considered, and for $LiFePO_4$ powder particles, it is lognormal [6,7], i.e., Gaussian along the logarithmic x-axis. In [8] it has been shown that the crushing of rocks results in just such a distribution of products, which is due to the multifactorial nature of the crushing process itself. For spherical particles

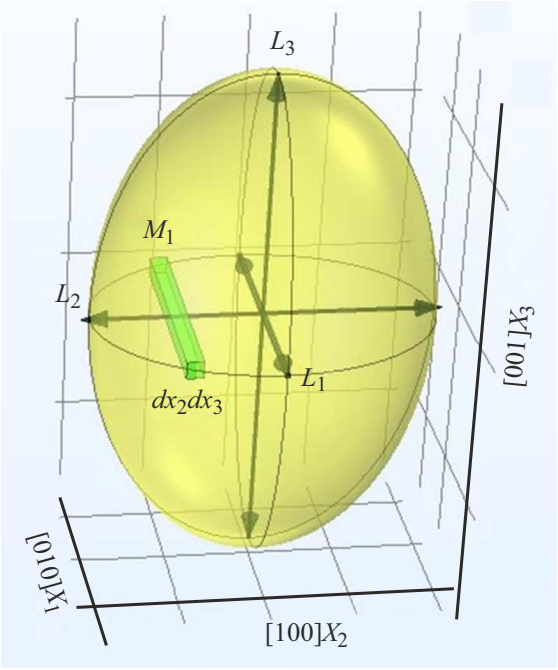

Figure 1. Ellipsoidal crystallite model with dimensions L_1, L_2 and L_3 along the [010], [100] and [001] axes, respectively. M_1 — length of column with cross section dx_2dx_3.

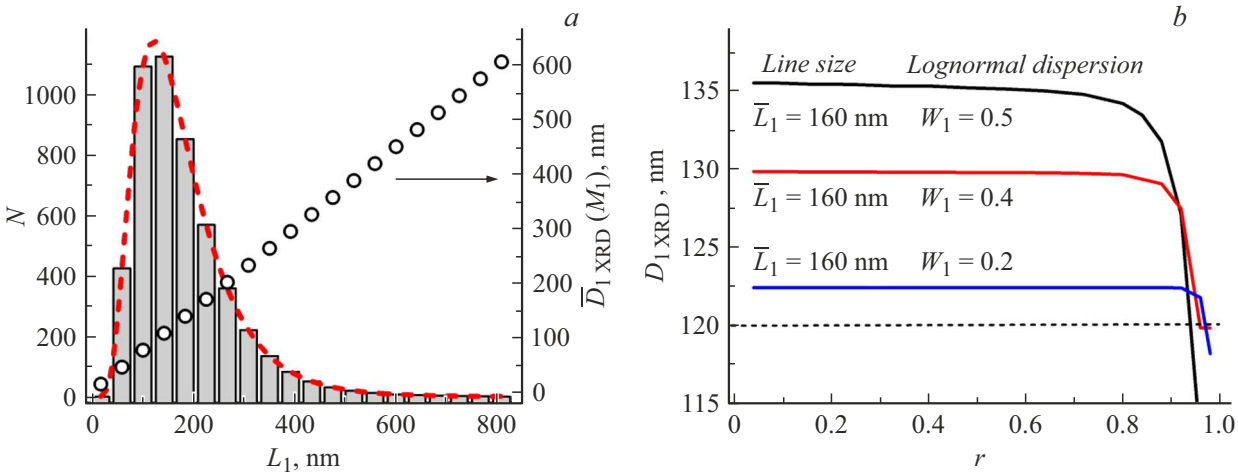

Figure 2. *a* — Simulation of the histogram of the marginal size distribution along the [010] axis and its approximation (dashed curve) by a lognormal distribution with parameters $\overline{L}_1 = 160$ nm, $W_1 = 0.5$, $r = 0.5$. The right axis corresponds to the column averaging calculations corresponding to each value of L_1.*b* — dependence of $D_{1\,\mathrm{XRD}}$ on the correlation coefficient r.

of diameter L, we use the following expression for this distribution:

$$f_1(L) = \frac{A}{\sqrt{2\pi}WL}\exp\left(-\frac{(\ln L/\overline{L})^2}{2W^2}\right), \tag{5}$$

where $\overline{L}$ — the mean of the lognormal distribution, W — its variance. For dispersed powders of crystallites $LiFePO_4$ [7], their distribution is described by the three-dimensional function $f(L_1, L_2, L_3)$ in the form of

$$f(\overline{L}) = \frac{1}{L_1L_2L_3\sqrt{(2\pi)^3 \det K}} \times \exp\left[-\frac{1}{2}\left(\ln\overline{L} - \ln\overline{\overline{L}}\right)^T\overline{\Lambda}^{-1}\left(\ln\overline{L} - \ln\overline{\overline{L}}\right)\right], \tag{6}$$

where

$$\overline{L} = \begin{bmatrix} L_1 \\ L_2 \\ L_3 \end{bmatrix}$$

— crystallite sizes,

$$\overline{\overline{L}} = \begin{bmatrix} \overline{L}_1 \\ \overline{L}_2 \\ \overline{L}_3 \end{bmatrix}$$

— their averages,

$$\overline{\Lambda} = \begin{bmatrix} W_1^2 & r_{12}W_1W_2 & r_{13}W_1W_3 \\ r_{21}W_2W_1 & W_2^2 & r_{23}W_2W_3 \\ r_{31}W_3W_1 & r_{32}W_3W_2 & W_3^2 \end{bmatrix}$$

— matrix of correlation moments, and the non-diagonal elements — the covariance between the marginal distributions (e.g., Cov_{12} — the covariance between the first and second marginal distributions), r_{12} — the correlation coefficient between them. The possible values of r_{12} are between zero and one. It is further shown that the computational results depend weakly on the coefficient r when its values are less than 0.8, and therefore we consider that $r_{12} = r_{13} = r_{23} = r$.

We make the assumption that the „X-ray diffraction" dimensions of $\overline{\overline{D}}_1(M_1)$ are the arithmetic mean averaging of $\overline{D}_1(M_1)$ by the function $f(\overline{L})$. To do this, we use the Mathematica 12 operator of matrix element multiplication and summation in the following form:

$$\overline{\overline{D}}_1(M_1) = Total\left[\overline{f} \circ \overline{D}_1(M_1)\right], \tag{7}$$

where L_{in}, L_{jn} and L_{kn} are used instead of $L_{1,2,3}$ from equations (2)–(4) — crystallite dimensions along the [010], [100] and [001] axes, respectively, the index n varies from 1 to N, and instead of V, the three-dimensional N-digit matrix of crystallite volumes $\overline{v} = \frac{\pi}{6}L_{in}L_{jn}L_{kn}$ is used from equation (1), each element of which is the volume of an ellipsoid, $\overline{f}$ — discretization of the function (6) normalized by one in the form of a matrix, each element of which is the probability of presence in the powder of an ellipsoid with the corresponding size.

To carry out calculations, let us consider that for industrial quality $LiFePO_4$ powders the parameters of the $f(\overline{L})$ function are in the following ranges: $\overline{L}_{1,2,3} \sim 40-200$ nm, $W_{1,2,3} \sim 0.3-0.6$, $r_{12,13,23} \sim 0.3-0.8$ [7]. Figure 2, *a* shows a simulation of a 20-bit histogram of the size distribution along the [010] axis (e.g., for 5000 digitized crystallites [6]). It has been verified that the number of digits should be at least 12 for small sampling error.

In Appendix, there are the numerical values of three-dimensional 5-digit matrices, the contents of which were used to control the steps of the calculation. The dependence of $D_{1\,\mathrm{XRD}}$ on L_1 is exactly the same as the last equality in equation (1) and, as can be seen in Fig. 2, *a*, is linear. Figure 2, *b* shows a very weak dependence of $D_{1\,\mathrm{XRD}}$ on r at $r < 0.8$, i.e., in the region of values observed for high quality samples $LiFePO_4$, but the effect of correlation coefficients

Electrochemical characteristics and particle sizes $LiFePO_4$

Ref. link	X-ray diffraction characteristics	Electrochemical characteristics at speed of discharge1 mA·h/g	
	Crystallite size, nm (XRD, SEM, TEM)	Diffusion constant, cm^2/s	Capacity , mA· h/g
[9]	200–800	$1.057 \cdot 10^{-14}$	149.3
[10]	50–100	$9.21 \cdot 10^{-13}$	115
[11]	300–400	$3.4 \cdot 10^{-14}$	151.3
[12]	~ 1000	10^{-10}–10^{-16} (simulation results)	
[13]	50–300	–	127
[14]	~ 100	–	115
[15]	300–700	$1.1 \cdot 10^{-14}$	90 (50%)
[16]	50–100	$0.12 \cdot 10^{-14}$	140

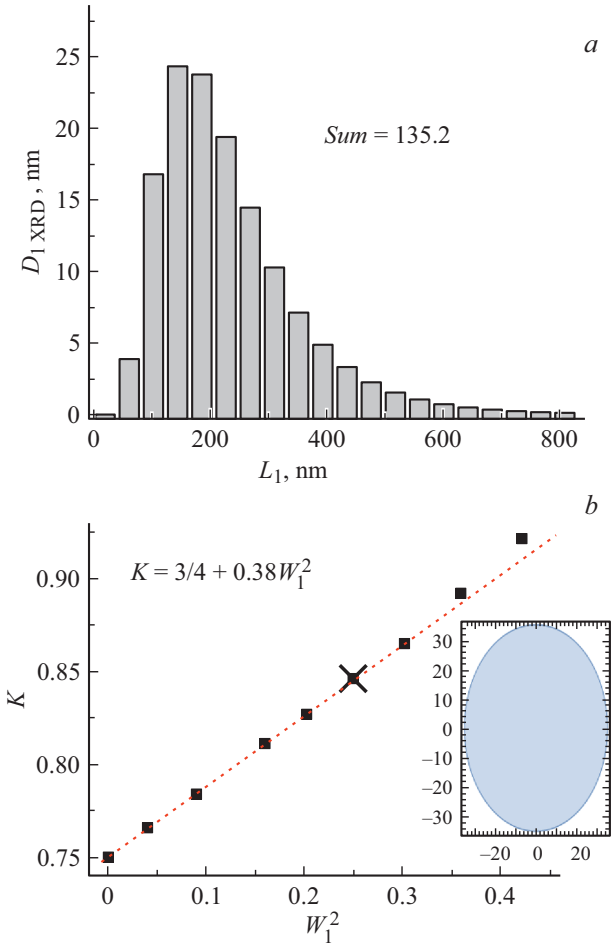

Figure 3. *a* — marginal distribution of „X-ray diffraction“ sizes over discrete values of L_1 and their sum according to equation (7) for dispersion $W = 0.5$ and $\bar{L}_1 = 160$ nm.*b* — normalized to $\bar{L}_1$ dependence of the correlation coefficient between $D_{i\,XRD}$ and $\bar{L}_i$ on the W_1^2 variance and its approximation (dashed line). The point marked with a cross corresponds to the histogram shown in part *a*. The inset — is an example of a region of double integration of (1) over the section of an ellipsoid.

on the magnitude of the electrochemical capacitance of powders [7] is quite significant.

Fig. 3, *a* shows the histogram of the „distribution of X-ray diffraction“ sizes. A shift to the larger size region can be seen, which is an indication of an increase in their averaging degree. The question arises as to the validity of the summation procedure for obtaining the desired result — the value of the „of the X-ray diffraction“ size of the powder as a whole. In fact, this summation has the same basis as the standard procedure of using integration in equation (1). The dependence of this sum normalized by $\bar{L}_1$, on the variance is shown in Fig. 3, *b*. It turned out to be described by a straight line in the range of actual W values (up to 0.6). If we use the well-known estimating equation

$$D_{1\,XRD} = \frac{3}{4}\bar{L}_V \approx \frac{3}{4}\frac{\Sigma_{i=1}^{N} L_i^4 p_i(L_i)}{\Sigma_{i=1}^{N} L_i^3 p_i(L_i)} \approx \frac{3}{4}\bar{L}_1 \exp\left(\frac{7}{2}W^2\right), \quad (8)$$

where the last equality corresponds to the case of lognormal size distribution, the appearance of W^2 arises naturally as a result of the exponent decomposing into a series for small W^2. However, in this case, the coefficient at this summand will be almost 10 times larger compared to the obtained value of 0.38.

Thus, the relation between the anisotropic „X-ray diffraction“ dimensions of $D_{i\,XRD}$ powder crystallites and their linear dimensions L_i in the following analytical form is obtained:

$$D_{i\,XRD} = \left(3/4 + 0.38W_i^2\right)\bar{L}_i. \quad (9)$$

The approximation using this relation is represented by the dashed line in Fig. 3, *b*. Noticeable deviations from equation (9) are observed in the region of dispersions $W > 0.6$ and correlation coefficients $r > 0.8$, which is beyond the values of these parameters in high quality powders $LiFePO_4$. Using equation (9), the error in the agreement of „of X-ray diffraction“ and linear dimensions can be reduced from 2% at $W \sim 0.2$ and to 15% at $W \sim 0.6$. The table presents literature data for electrochemical performance as a function of particle size.

Conflict of interest

The authors declare that they have no conflict of interest.

Appendix. Illustration of numerical values of three-dimensional 5-digit matrices

$L_{1,2,3}$ values for a 5-bit matrix

19	$\frac{867}{4}$	$\frac{829}{2}$	$\frac{2449}{4}$	810
9	$\frac{211}{2}$	202	$\frac{597}{2}$	395
9	$\frac{211}{2}$	202	$\frac{597}{2}$	395

Correlation matrix

0.25	0.125	0.125
0.125	0.25	0.125
0.125	0.125	0.25

Here $W_1^2 = W_2^2 = W_3^2 = 0.25$, $r_{12} = r_{13} = r_{32} = 0.5$.

The third and fourth rows of the 5-digit matrix of the lognormal distribution function $f(\bar{L})$ normalized to one:

$4.74 \cdot 10^{-11}$	$7.22 \cdot 10^{-9}$	$8.54 \cdot 10^{-11}$	$1.82 \cdot 10^{-12}$	$6.7 \cdot 10^{-14}$
$7.22 \cdot 10^{-9}$	0.071	0.0162	0.00205	0.000271
$8.54 \cdot 10^{-11}$	0.0162	0.00814	0.00166	0.000308
$1.82 \cdot 10^{-12}$	0.00205	0.00166	0.000452	0.000103
$6.7 \cdot 10^{-14}$	0.000271	0.000308	0.000103	0.0000272
$1.06 \cdot 10^{-13}$	$9.59 \cdot 10^{-11}$	$1.82 \cdot 10^{-12}$	$5.19 \cdot 10^{-14}$	$2.34 \cdot 10^{-15}$
$9.59 \cdot 10^{-11}$	0.0056	0.00205	0.000347	0.0000561
$1.82 \cdot 10^{-12}$	0.00205	0.00166	0.000452	0.000103
$5.19 \cdot 10^{-14}$	0.000347	0.000452	0.000163	0.0000457
$2.34 \cdot 10^{-15}$	0.0000561	0.000103	0.0000457	0.0000148

The third and fourth rows of the 5-digit matrix $\bar{D}_1(M_1)$ of column averaging over crystallite volumes are given next. For example, we can see that for an ellipsoid with $L_1 = 414.5$ for D_1 we obtain $D_1 = 0.75(829/2) \approx 310.9$. This value is independent of L_2 and L_3:

310.9	310.9	310.9	310.9	310.9
310.9	310.9	310.9	310.9	310.9
310.9	310.9	310.9	310.9	310.9
310.9	310.9	310.9	310.9	310.9
310.9	310.9	310.9	310.9	310.9
459.2	459.2	459.2	459.2	459.2
459.2	459.2	459.2	459.2	459.2
459.2	459.2	459.2	459.2	459.2
459.2	459.2	459.2	459.2	459.2
459.2	459.2	459.2	459.2	459.2

For the third and fourth rows of the 5-bit piecewise product matrix $(\bar{f} \circ \bar{D}_1(M_1))$, the sum of all elements of the matrix $\bar{f}$ is normalized to one:

$1.47 \cdot 10^{-8}$	$2.25 \cdot 10^{-6}$	$2.66 \cdot 10^{-8}$	$5.67 \cdot 10^{-10}$	$2.08 \cdot 10^{-11}$
$2.25 \cdot 10^{-6}$	22.1	5.03	0.638	0.0842
$2.66 \cdot 10^{-8}$	5.03	2.53	0.517	0.0958
$5.67 \cdot 10^{-10}$	0.638	0.517	0.14	0.032
$2.08 \cdot 10^{-11}$	0.0842	0.0958	0.032	0.00845
$4.86 \cdot 10^{-11}$	$4.4 \cdot 10^{-8}$	$8.38 \cdot 10^{-10}$	$2.38 \cdot 10^{-11}$	$1.08 \cdot 10^{-12}$
$4.4 \cdot 10^{-8}$	2.57	0.943	0.159	0.0258
$8.38 \cdot 10^{-10}$	0.943	0.763	0.207	0.0472
$2.38 \cdot 10^{-11}$	0.159	0.207	0.075	0.021
$1.08 \cdot 10^{-12}$	0.0258	0.0472	0.021	0.00681

References

[1] W.L. Smith, J. Appl. Cryst., **9** (3), 187 (1976). DOI: 10.1107/S0021889876010923

[2] J.I. Langford, A.J.C. Wilson, J. Appl. Cryst., **11** (2), 102 (1978). DOI: 10.1107/S0021889878012844

[3] R.J. Matyi, L.H. Schwartz, J.B. Butt, Catal. Rev. Sci. Eng., **29** (1), 41 (1987). DOI: 10.1080/01614948708067547

[4] C.E. Krill, R. Birringer, Phil. Mag. A, **77** (3), 621 (1998). DOI: 10.1080/01418619808224072

[5] T.B. Žunić, J. Dohrup, Powder Diffr., **14** (3), 203 (1999). DOI: 10.1017/S0885715600010538

[6] A. Bobyl, I. Kasatkin, RSC Adv., **11** (23), 13799 (2021). DOI: 10.1039/D1RA02102H

[7] A. Bobyl, S.C. Nam, J.H. Song, A. Ivanishchev, A. Ushakov, J. Electrochem. Sci. Technol., **13** (4), 438 (2022). DOI: 10.33961/jecst.2022.00248

[8] A.N. Kolmogorov, DAN, **31** (2), 99 (1941).

[9] D. Meng, H. Duan, Sh. Wu, X. Ren, Sh. Yuan, J. Alloys Compd., **967**, 171570 (2023). DOI: 10.1016/j.jallcom.2023.171570

[10] D.V. Trinh, M.T.T. Nguyen, N.T.L. Huynh, H.V. Tran, Ch.D. Huynh, Arab. J. Sci. Eng., **48** (6), 7713 (2023). DOI: 10.1007/s13369-023-07799-5

[11] X. Shen, Z. Qin, P. He, X. Ren, Y. Li, F. Wu, Y. Cheng, Z. He, Coatings, **13** (6), 1038 (2023). DOI: 10.3390/ coatings13061038

[12] A.V. Churikov, A.V. Ivanishchev, I.A. Ivanishcheva, V.O. Sycheva, N.R. Khasanova, E.V. Antipov, Electrochim. Acta, **55** (8), 2939 (2010). DOI: 10.1016/j.electacta.2009.12.079

[13] S. Yaroslavtsev, S. Novikova, V. Rusakov, N. Vostrov, T. Kulova, A. Skundin, A. Yaroslavtsev, Solid State Ion., **317**, 149 (2018). DOI: 10.1016/j.ssi.2018.01.011

[14] F. Cheng, W. Wan, Z. Tan, Y. Huang, H. Zhou, J. Chen, X. Zhang, Electrochim. Acta, **56** (8), 2999 (2011). DOI: 10.1016/j.electacta.2011.01.007

[15] A.V. Ivanishchev, I.A. Ivanishcheva, A. Dixit, Russ. J. Electrochem., **55** (8), 719 (2019). DOI: 10.1134/S102319351908007X.

[16] D. Agafonov, A. Bobyl, A. Kamzin, A. Nashchekin, E. Ershenko, A. Ushakov, I. Kasatkin, V. Levitskii, M. Trenikhin, E. Terukov, Energies, **16** (3), 1551 (2023). DOI: 10.3390/en16031551

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