Benchtop XRD for Battery Cathode Materials

1. Background

Cathode materials have an integral function in lithium-ion batteries by reversibly hosting cationic lithium ions, which move between the cathode and anode through intercalation and deintercalation during charging and discharging. The specific capacity and structural stability of cathode materials directly affect the performance of lithium-ion batteries. Current commercial cathode materials can be divided into three structural categories: layered structures like $LiMO_2$ (M = Co, Ni, Mn), spinels such as $Li_2M_2O_4$ (M = Ni, Mn), and olivine compounds like $LiMPO_4$ (M = Co, Ni, Mn, Fe). Specifically, olivine-type $LiFePO_4$ cathodes have attracted attention due to their low toxicity, low cost, and long cycling ability.(1) Olivine $LiFePO_4$ cathode materials were first reported by the Goodenough research group in 1997.(2) Although the open circuit voltage of this material was lower than that of manganese and cobalt-based materials, it demonstrated reversible extraction and insertion of Li with a specific capacity of 110 mAh/g.(2) These advantages have made olivine $LiFePO_4$ an attractive cathode material for lithium-ion battery development.

$LiFePO_4$ belongs to the orthogonal crystal system (space group Pnma), and the crystal structure is shown in Figure 1. Since the unit cell parameters of $FePO_4$ are very similar to the $LiFePO_4$ unit cell, the de-embedding of Li^+ during charging and discharging is unlikely to deform the overall olivine crystal structure.

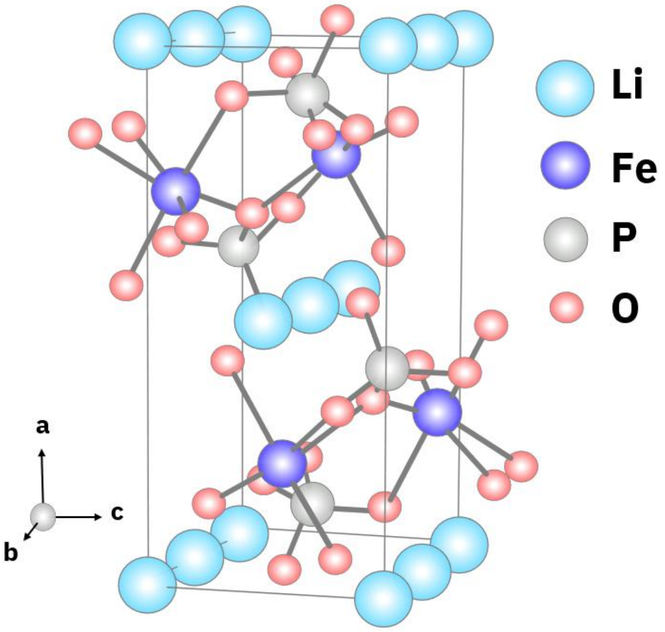


Figure 1: Crystal structure for olivine $LiFePO_4$

However, $LiFePO_4$ suffers from sluggish Li intercalation/deintercalation kinetics and poor electronic conductivity, which greatly constrain its practical application. To solve this, the structure of $LiFePO_4$ can be modified to enhance the conductivity and improve the mobility rate of lithium ions.

Modified $LiFePO_4$ can be characterized by the changes in crystal structure, namely unit cell parameters (*a*, *b*, and *c*) and unit cell volume (V). In $LiFePO_4$ materials, the bond length of P-O determines the structural stability. Shorter P-O bonds correspond with stronger bond energy and higher stability, which improves the cycling performance of the material. Additionally, the strength of the Li-O bond determines the ease of de-intercalation of Li. Weaker Li-O bonds allow for easier lithium removal, which improves the kinetics for faster charging/discharging.

X-ray diffraction (XRD) is the most effective and widely used characterization method for studying the crystal structure of matter. It works by irradiating X-rays of specific wavelengths from different angles through the crystal, and when rays with different angles of incidence pass through the crystal plane, diffraction occurs at a specific angle. The crystallinity, unit cell volume, grain size and other material information can be obtained by recording the diffraction angle and the diffraction peak intensity at that angle. Therefore, XRD is a conventional means of qualitative and quantitative analysis of the phases in electrode materials. More importantly for modified $LiFePO_4$, there will inevitably be slight changes to the crystal structure. XRD Rietveld refinement plays an important role in establishing the structure-effect relationship of materials by obtaining structural information such as phase ratio, unit cell parameters, proportion of key atoms, and atomic coordinates.

2. Experimental Methods

In this application note, the crystal structure and phase composition of $LiFePO_4$ samples were characterized by the **AMI Lattice Pro X-ray diffractometer** (Cu target, λ=0.1548nm). The 2θ angle characterization range was 10~90°. In addition, the material structure of the XRD spectra was refined by Rietveld's Whole Pattern Fitting (WPF) method, and the unit cell parameters and crystal structure were calculated.

3. Results and Discussion

As shown in Figure 2a, the $LiFePO_4$ powder sample showed sharp diffraction peaks consistent with the standard card of orthogonal crystalline $LiFePO_4$ (PDF#97-016-5000), indicating that the sample had an olivine crystal structure and excellent crystallinity. Therefore, the crystal form and corresponding crystallinity of modified lithium iron phosphate can be analyzed by diffraction spectra.

To further investigate the crystal structure of lithium iron phosphate, the XRD diffraction spectrum was analyzed with the Whole Pattern Fitting (WPF) method, shown in Figure 2b and Table 1. First, the

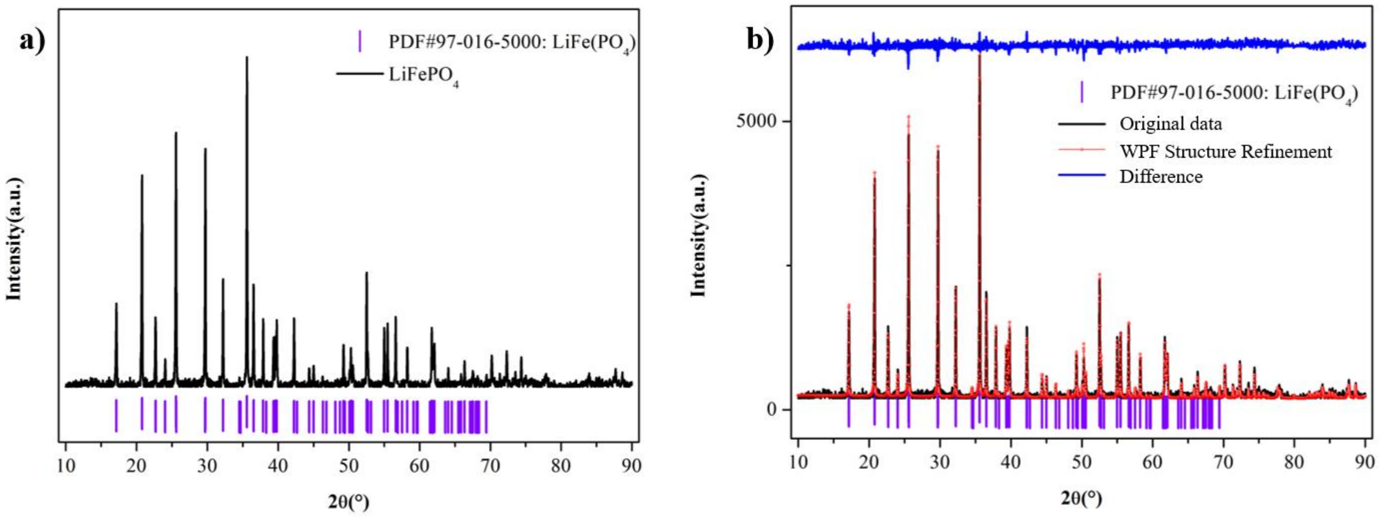


Figure 2: a) Experimental XRD pattern of $LiFePO_4$ compared to standard $LiFePO_4$ (PDF: 97-016-5000) and b) experimental $LiFePO_4$ (black line) overlayed with WPF structure refinement results (red line) and the difference line (blue line).

unit cell parameters a, b, and c of $LiFePO_4$ were determined, and the corresponding unit cell volume V was calculated. These values can serve as a baseline for comparison against modified $LiFePO_4$.

The coordinates of each atom of $LiFePO_4$ were obtained through structural refinement, shown in Table 2. This model can be used to determine the specific crystal structure of the original $LiFePO_4$, and then the structural changes after modification can be carefully compared to the reference material.

Sample	**Unit Cell Parameters**			
	a (Å)	b (Å)	c (Å)	V (Å^3)
$LiFePO_4$	10.32575	6.00599	4.69098	290.9

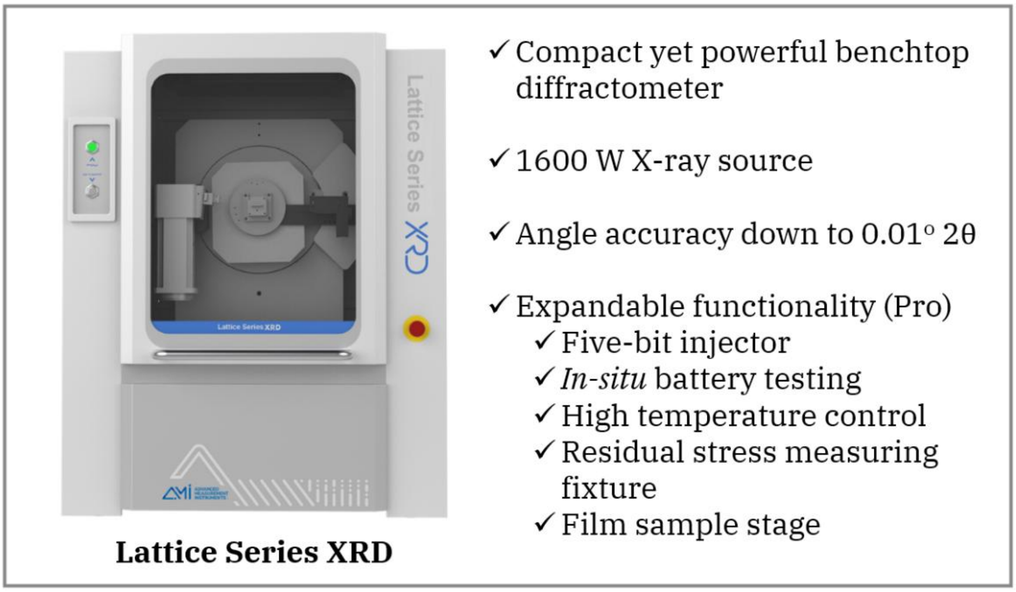
Table 1: Unit cell parameters for $LiFePO_4$ calculated using the WPF method

Label	Charge	Scattering	Occupancy	x	y	z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Li 1	Li +1	4	1	0	0	0	0.022	0.019	0.0156	-0.0027	-0.002	-0.0053
Fe 1	Fe +2	4	1	0.28195	1/4	0.97173	0.0043	0.0045	0.0062	0.0	0.0003	0.0
P 1	P +4	4	1	0.09588	1/4	0.42434	0.0036	0.0036	0.0035	0.0	0.0003	0.0
O 1	O -2	4	1	0.09446	1/4	0.71872	0.0084	0.0075	0.0029	0.0	-0.0005	0.0
O 2	O -2	4	1	0.46315	1/4	0.20888	0.0038	0.008	0.0065	0.0	0.0003	0.0
O 3	O -2	4	1	0.16247	0.05539	0.28653	0.0085	0.0048	0.0064	0.0034	0.0011	-0.0005

Table 2: Atomic coordinates of $LiFePO_4$ obtained with the WPF method

4. Conclusions

XRD techniques are useful for investigating the atomic structure of cathode materials for lithium-ion batteries. XRD can describe key structural information like unit cell parameters, atomic coordinates, and bond lengths, all of which can affect the stability and electrochemical activity of cathode materials. The **Lattice Pro XRD** from AMI, shown in Figure 3, combines compact benchtop capabilities with precise, high-performance analysis of battery materials. The **Lattice Pro XRD** is designed for simple powder analysis and complex research problems, offering expandable functionality with *in-situ* battery test accessories.



Lattice Series XRD

- ✓ Compact yet powerful benchtop diffractometer
- ✓ 1600 W X-ray source
- ✓ Angle accuracy down to 0.01° 2θ
- ✓ Expandable functionality (Pro)
  - ✓ Five-bit injector
  - ✓ *In-situ* battery testing
  - ✓ High temperature control
  - ✓ Residual stress measuring fixture
  - ✓ Film sample stage

Figure 3: Overview of Lattice Series XRD from AMI

5. References

(1) Wang, Y.; He, P.; Zhou, H. Olivine $LiFePO_4$: Development and future. *Energy Environ. Sci.,* **2011**, *4*, 805-817.

(2) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.*, **1997**, *144*, 1188.