Ab-initio Calculation of the XANES of Lithium Phosphates and LiFePO_4

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Abstract
Lithium iron phosphate has been regarded as a promising cathode material for the next generation lithium ion batteries due to its high specific capacity, superior thermal and cyclic stability [1]. In this study, the XANES (X-ray Absorption Near Edge Structure) spectra of lithium iron phosphate and lithium phosphates of various compositions at the Li K, P L_3,2, Fe M_3,2 and O K-edges have been simulated self-consistently using ab-initio calculations based on multiple scattering theory (the FEFF9 code) and DFT (Density Functional Theory, the Wien2k code). The lithium phosphates under investigation include LiFePO_4, γ-Li_3PO_4, Li_4P_2O_7 and LiPO_3. The calculated spectra are compared to the experimental XANES recorded in total electron yield (TEY) and fluorescence yield (FLY). This work was carried out to assess the XANES of possible phases presented in LiFePO_4 based Li ion battery applications [2].

1. Introduction
Currently, lithium-ion batteries employ LiCoO_2 as cathode material and carbon as anode material. This limits applications to small-scale batteries due to the high cost and toxicity of Co [3]. In recent years, lithium iron phosphate (LiFePO_4) has been considered to be a potential cathode material for rechargeable lithium ion batteries due to its high specific capacity (170 mAh/g) and a discharge voltage of 3.4 V between loading of Li^+ versus Li. [4]. LiFePO_4 becomes desirable for the next generation of Li-ion cells over LiCoO_2 because of its low raw material cost, environmental friendliness and excellent cycling capacity. The key limitation of this material has been extremely low electronic conductivity (10^-9 S/cm). It has been reported that either particle size reduction or coating with carbon or metal ion doping greatly enhances the electrochemical behavior [5].

2. Theory
2.1. Multiple Scattering Theory - Calculation by FEFF9
The XANES (X-ray Absorption Near Edge Structure) spectra of these Li compounds with the above-mentioned crystal models have been calculated by the self-consistent multiple scattering theory using the FEFF9 code [6]. This theory is based on the real-space Green’s function approach [7]. The FEFF code is arranged in primary subroutines that correspond to the calculation of XAFS [8]. First it calculates the atomic potentials and densities. Then it generates a muffin-tin scattering potential that includes the excited-state self-energy and calculated energy reference. It also calculates the complex partial wave phase shifts. Finally, it computes the curved-wave scattering amplitudes and phase shifts and the exact single-scattering curved -wave XAFS spectra.

2.2 DFT and GGA Theory - Calculation by WIEN2k
The theoretical XANES spectra are also calculated self-consistently by the Density Functional Theory (DFT) with Generalized Gradient Approximation (GGA) using the WIEN2k program [9]. Full potential augmented plane wave method has been used in the numerical calculation. The code has been built based on the Density Functional Theory [10] which provides an ab-initio method of calculating matters with a relatively homogenous distribution of electrons around the atomic sites. It further uses the Generalized Gradient Approximation [11] to contribute a first derivative correction to DFT. Crystals are described by the unit cell which have atoms occupying the symmetric atomic sites with interstitial area. Atomic sites are spheres of bases, which are generated by a set of non-overlapping spherical harmonics $Y_{lm}$. The interstitial regions are expressed by set of plane waves. The set of plane waves, $e^{ikr}$, has been extended to 20000 plane waves in the calculation of the systems in the present work. The boundary condition between the atomic sites and the interstitial area satisfies the Dirichlet condition. Scalar relativistic density function was used with GGA correction. Self-consistent minimization of energy was achieved with 1000 k points to keep a better accuracy in each calculation. The theoretical XANES spectra have been calculated using the electrical dipole transition given by the selection rule of $\Delta l = \pm 1$ ($l$ is the angular momentum quantum number) and convoluted by instrumental Gaussian and core-hole lifetime Lorentzian broadenings [12].

2.3 Structures of the Li phosphate crystals

The Li compounds, LiFePO$_4$, $\gamma$-Li$_3$PO$_4$, Li$_4$P$_2$O$_7$, and LiPO$_3$ have been modelled as crystals with structural symmetries of Pnma [13], Pmnb [14], P-1 [15], and P2/n [16] respectively. The crystal constants and geometries of these Li compounds are listed in table 1. LiFePO$_4$ has an olivine structure, in which Li, Fe, and P atoms occupy 4a, 4c, and 4c sites, respectively.

|                  | a (Å)  | b (Å)  | c (Å)  | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|------------------|--------|--------|--------|--------------|-------------|--------------|
| LiFePO$_4$       | 10.332 | 6.01   | 4.692  | 90           | 90          | 90           |
| $\gamma$-Li$_3$PO$_4$ | 6.1113 | 10.4612| 4.9208 | 90           | 90          | 90           |
| Li$_4$P$_2$O$_7$ | 8.5613 | 7.11   | 5.1851 | 111.441      | 89.986      | 103.065      |
| LiPO$_3$        | 13.074 | 5.4068 | 16.452 | 90           | 99          | 90           |

3. Experiment

All the samples are very fine powders from Phosotech Lithium Inc. The XANES measurements were performed at the Canadian Light Source (CLS) on the Variable Line Spacing Plane Grating Monochromator (VLS PGM) beam-line for the Li K-edge and P L$_{3,2}$-edge spectra, and the high resolution Spherical Grating Monochromator (SGM) beam-line for the O K-edge and Fe L$_{3,2}$-edge spectra. Spectra were recorded in fluorescence yield (FLY) using a micro-channel plate detector and total electron yield (TEY) by measuring the sample current with a current amplifier.

4. Results and Discussions

XANES spectra are characterized by intense resonance features, arising from excitations of core-level electrons to unoccupied orbitals that are bound, quasi-bound and continuum levels following mainly electrical dipole transition. The XANES spectra of Li K edges, P L$_{3,2}$ edges, O K edges, and Fe M$_{3,2}$ edges of the Li compounds as described by the above-mentioned crystal structures have been calculated numerically by FEFF9 and WIEN2k self-consistently. The calculated results together with the experimental spectra are plotted in figure 1 to 3. All experimental spectra reported were normalized to one after divided by the intensities of the incident beam ($I_0$), which have been measured simultaneously with a refreshed gold mesh located after the last optical elements of the beam-line.

The selection rule for the dipole transition follows $\Delta l = \pm 1$, $|J| = 0, \pm 1$ where $l$ and $j$ are the orbital and spin-orbit quantum numbers, respectively. Thus Fe M$_{3,2}$ (3p) and L$_{3,2}$-edge (2p) probe the unoccupied states of Fe 3d and 4s character. The Li and O K-edges (1s) probe the unoccupied states of
the p character of Li and O respectively. The P L_{3,2} edge probes states of s and d characters of P. The

Figure 1. The experimental and theoretical XANES at Li K-edge of LiFePO₄, γ-Li₃PO₄, Li₄P₂O₇, and LiPO₃.

Figure 2. The experimental and theoretical XANES at P L_{3,2}-edge of LiFePO₄, γ-Li₃PO₄, Li₄P₂O₇, and LiPO₃.

Figure 3. The experimental and theoretical XANES at O K-edge of LiFePO₄, γ-Li₃PO₄, Li₄P₂O₇, and LiPO₃.

partial densities of state of Li and Fe of LiFePO₄ have also been evaluated by WIEN2k. The peak positions of the XANES of the Li compounds are shown by the arrows in figure 1 to 3. In figure 1, the peaks A', B' and C' of LiFePO₄ are due to the Fe M_{3,2} edges XANES of LiFePO₄. The calculated spectra from FEFF has been shifted 2 eV to fit the experimental Fe M_{3,2} edge of LiFePO₄. The calculated XANES of the Li compounds are shown by the arrows in figure 1 to 3. In figure 1, the peaks A, B and C follow the same trends. The A, B and D peaks of the experimental P L_{3,2} XANES smooth out in the FEFF 9 calculation due to the finite sizes

of the crystal clusters of about 50 atoms constrained by the full multiple scattering. All the theoretical XANES spectra show there are peaks around 160 eV for these model Li phosphates. In figure 3, the theoretical O K XANES of the Li compounds compose the average O K edges from different symmetric sites of O in the crystals. There are 3, 3, 7, and 15 O symmetric sites in LiFePO$_4$, $\gamma$-Li$_3$PO$_4$, and Li$_2$P$_2$O$_7$, and LiPO$_3$, respectively. The A peaks of the GGA calculated O K XANES spectra are higher than that of the experimental TEY spectra and show that the effect of the local environment of the O sites contributes substantially to the theoretical spectra. TEY measurements are surface sensitive, since low energy electrons have a short escape depth, while the x-ray fluorescent yield is bulk sensitive unless the sample is thick and self absorption occurs. The discrepancy between the TEY of the O K-edge and the calculated spectra by FEFF9 is due to the small cluster sizes for the FEFF calculation and the surface oxides of the samples which deviate from the crystal models.

5. Conclusion
XANES probes the local structure and bonding of the absorbing atom in a chemical environment and is element specific. Thus it can provide information of the local environment of Li and other elements of these Li phosphate compounds, in particular LiFePO$_4$, to help the design of future batteries. XANES simulation provides a useful tool to investigate the subtle variation of the local environment.

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