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XAFS Calculations of Nd-Substituted $LiFeO_2$ Material

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ABSTRACT. $LiFeO_2$ (LFO) is a well-known battery cathode material with its popular use in commercial batteries. In this study, Nd^{3+} ions were substituted in Fe^{3+} ions coordination to probe the electronic interplay between the 3*d* and 4*f* levels and their electronic influence on each other. The electronic properties of the LFO material with rare earth Nd-substitution were studied according to the general formula; "$LiFe_{1-x}Nd_xO_2$", where x has values of 0.00, 0.10, and 0.20, respectively. Apart from the transition metals, the lanthanide Nd^{3+} ion has unoccupied 4*f* levels that can provide convenient quantum symmetries for the *d*-levels and electrons to build up a playground for the electronic interplay. The study was carried by the x-ray absorption fine structure (XAFS) spectroscopy calculations. The results showed a possible application of Nd-substitution can yield better cathode properties in Li-ion battery devices.

KEYWORDS. Crystal structure; Electronic structure; Li-ion batteries; Absorption spectroscopy.

INTRODUCTION. Parallel to the development in electromechanical technology, research studies on high-quality energy storage systems needed by mobile devices has been gaining momentum day by day.[1-3] By this means, rechargeable batteries with high power and high-performance became the most prominent energy storage devices in use and Li-ion batteries are pioneers of rechargeable batteries. In this sense, these batteries, which entered the literature and commercial markets with $LiCoO_2$ material, are now concentrated around $LiMnO_2$ and $LiFeO_2$ (LFO) main materials. The main factor for these materials to come to the fore is their cheap metals and their high-performance values. However, these popular materials have also produced some undesirable defects such as temperature-related performance degradation and voltage loss over long cycles. In this respect, the main focus of scientific studies is to improve these undesirable conditions, which is essential for current modern technologies.

$LiFeO_2$ has been studied for many years as an alternative to $LiCoO_2$ cathode. However, one of main challenge in this studies is the various crystalline structure of LFO exhibits.[4] In this study, the cation-disordered α-$LiFeO_2$ phase (Fig. 1) is studied with rare-earth neodymium LFO material by the x-ray absorption fine structure (XAFS) spectroscopy as a useful technique to achieve the purpose.[4-6] α-$LiFeO_2$ has cubic structure with *Fm3m* space group.

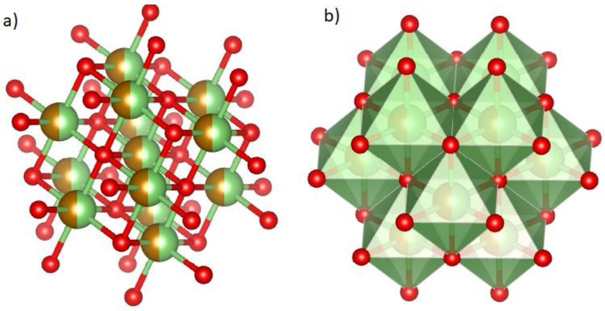

Fig. 1: a) Crystal structure of α-$LiFeO_2$, b) Octahedral site symmetry view.[7]

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Employing the XAFS technique calculations, the influence of neodymium (Nd) atom substitution on both the crystal and electronic structure of Fe atoms in the LFO material were investigated.

METHODOLOGY. This work was done based on advantage of employing computer-based calculations for investigating materials at the atomic and molecular scales.[8-13] The electronic properties of α-LiFe$_{1-x}$Nd$_x$O$_2$ (x= 0.00, 0.10, and 0.20) materials have been studied by performing XAFS calculations. In the calculations, one Fe atom was chosen as the source atom in the calculated materials, and the parent LFO was used as the reference material. Calculations were performed using the real-space multiple scattering approach FEFF8.20 code.[14, 15] For the calculations, input files were generated using the TkAtoms package. For the calculations, an input file has been created for the α-LiFeO$_2$ material in cubic structure with *Fm3m* space group for 10 Å thick cluster, containing 251 atoms (Li, Fe, and O) with the lattice parameters; a: 4.157 Å and O^{2-} (x, y, z): (0.0, 0.0, 0.0: occupancy 1.0), Fe^{3+} (0.5, 0.5, 0.5: occupancy 0.5), and Li^{+} (0.5, 0.5, 0.5: occupancy 0.5). For Nd-substitution, Na atoms were replaced in Fe atoms coordination according to the substitution amounts and calculations were performed at the room temperature.

RESULTS & DISCUSSION. The substitution of an atom in host coordination may cause defects, distortions or may become a part of the crystal structure. Sometimes, even defects or distortions could be treated as a gift promoting the desired properties of the materials.[16-19] To study the properties of materials, the XAFS technique has an important place to investigate the characteristics of elements in detail.[20] The reason for the popularity of the XAFS technique in scientific researches comes from that it provides information about the electronic structure, molecular interplays, chemical bonding, electronic spin properties, and also contains crystal properties.[21-23] To examine the XAFS spectrum in two main parts is a common way of analysis: X-ray Near Edge Absorption Spectroscopy (XANES) and Extended XAFS (EXAFS). The XANES region spectra are related to the traces of the electronic (bond) interactions with the neighbors of the target atom in absorption spectroscopy, while the EXAFS part (approximately 40 ~ 80 eV above the main absorption edge) gives the atomic arrangements around the source atom via the fluctuating spectra which is due to the scattering interactions of the photoelectrons.

In the LFO cathode material, Fe atoms possess Fe^{3+} ionic state, while Li atoms possess Li^{+} ionic state. The ground state electronic configuration of Fe metal is [Ar]$4s^2 3d^6 4p^0$ and Fe^{3+} ion possess [Ar]$4s^2 3d^3 4p^0$. The ground state electronic configuration of the substituted Nd atom is [Xe]$4f^4 6s^2$, and Nd^{3+} is [Xe]$4f^3 6s^0 5d^0 6p^0$. The narrow but electron rich "*f*" levels are the key role player of the molecular interactions in the atomic media.[24] Because, as seen in the electronic configuration of the Nd^{3+} ion, they can provide rich quantum symmetry opportunities to any electrons that can take place in a molecular bonding mechanism. As being the host and the main metal of the LFO material, we focused to probe the electronic properties of the Fe atoms. Fe K-edge absorption spectra of the LiFe$_{1-x}$Nd$_x$O$_3$ material is given in Fig. 2.

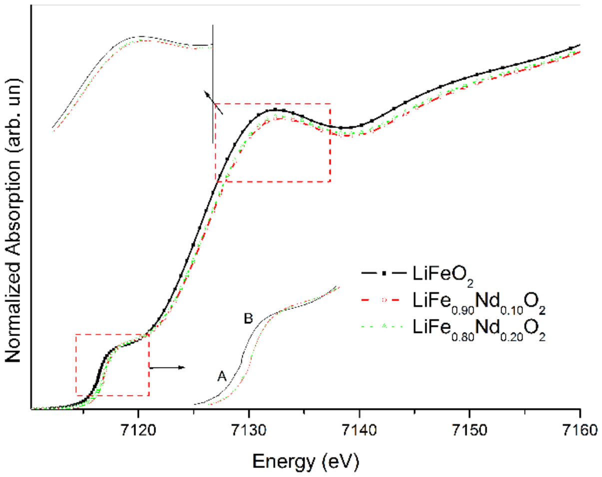

Fig. 2: Compared Fe K-edge XANES spectra of the parent and Nd-substituted LiFeO$_2$ cathode materials.

The K-edge XAFS spectra of Fe atom correspond to the transition of the excited 1*s* electrons to an unoccupied valence level. However, there are rules that those electrons should obey, i.e., quantum selection rules, Δl=±1. For Fe atoms, the valence level is the unoccupied 3*d* level. But 1*s* electrons avoid locating into the 3*d* level as a final state due to the quantum selection rules and make their transition to the empty 4*p* levels. The energy difference between the forbidden unoccupied 3*d* and available 4*p* levels cause a slope on the absorption spectra.

In Fig. 2, Fe K-edge absorption spectra raised at 7112 eV and a shoulder like pre-edge structure appeared just above the rising slope of the spectra at 7118 eV. The pre-edge structure is a result of the forbidden transitions that do not obey the quantum selection rules and is a quadrupole transition for transition metals. The transition of the excited 1*s* electrons should be the unoccupied 4*p* levels and the pre-edge feature points out some transitions are finalized at forbidden 4*s* and 3*d* levels. A pure 3*d* or 4*s* level does not accept *s*-electrons to any energy level, unless a mixing or hybridization occurs. The pre-edge addresses a hybridized molecular level formation between Fe 4*s* - O 2*p* and Fe 3*d* - O 2*p*, where a level containing both with *s*, *d*, and *p* quantum symmetries. This edge emphasizes a strong molecular interaction between Fe and O atoms. A strong pre-edge peak also means strong bonding between Fe-O and weak bonding between Li-O. Thus, it also points out why $LiFeO_2$ material is good cathode material and reveals good intercalation mechanisms. The traces of the electronic interplay can be seen in Fig. 3 with the calculated density of states (DOS).

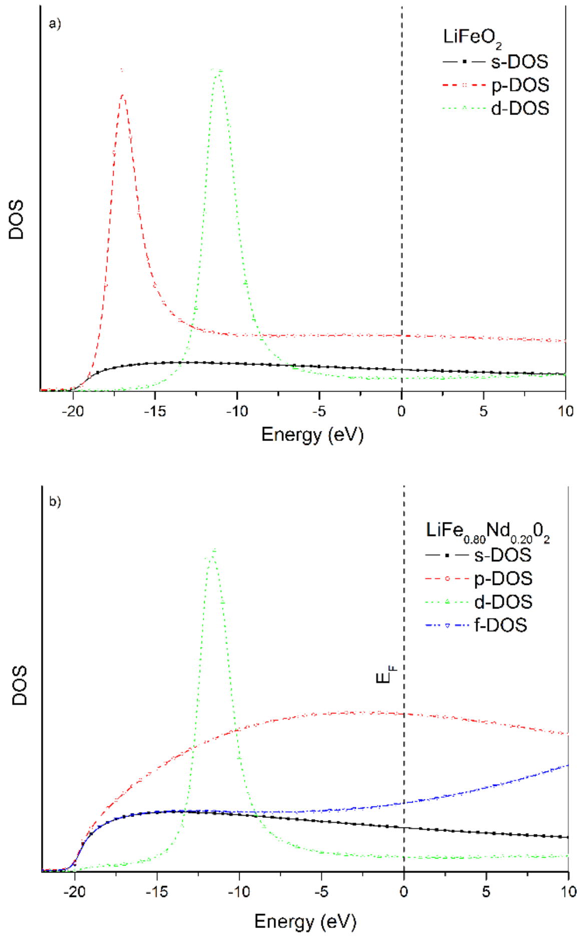

Fig. 3: Density of states (DOS) of a) $LiFeO_2$, b) $LiFe_{0.80}Nd_{0.20}O_2$.

According to Fig. 3a, the narrow *d*-band points out the restricted band structure and O *p*-band located below the *d*-band due to the transition from the *s*-level and the electrons transferred during the bonding between Fe-O. O 2*p* level seems to have a hybridization with the *s*-band which is placed as a pre-edge peak assigned as "A". The broader pre-edge is related to the oxygen 2*p* and iron 3*d* hybridization. The tail part of the energy densities is open emphasizing the possibility to fill up the levels with possible transitions or with inner shell excitations. In Fig. 3b, the density of states of 20 % Nd-substituted LFO material, the 4*f* level has also a contribution and the level has stated below the Fermi level. With the presence of the *f*-level, *p*-level became stronger and energy values of both *f*-level and *s*-level have a high agreement. The increase in DOS intensity of *p*-level points out stronger activity in molecular levels and *f*-level has a weak overlap with *d*-level that shifted the *d*-level 0.23 eV below than the DOS given in Fig. 3a. The only possibility of the *f*-level interplay is with the *d*-level due to quantum selection rules. The reflection of this interaction on the absorption spectra, Nd-substituted materials data should be focused.

For the Nd-substituted materials, a high agreement on the XAFS spectra seen. The agreement emphasizes electronically adapted Nd atoms in Fe environment and did not ruin the crystal structure even its larger volume. The main absorption edge of the LFO material was determined at 7131.9 eV which is a result of 1*s* → 4*p* transitions. The spectra of Nd-substituted materials has very high agreement on peak structures. However, an energy shift of about 0.7 eV was observed to higher energy values for the Nd-substituted materials. The hybridization interplay between *s*-*p*-*d*-*f* levels seems to push the 4*p* level to higher energy.

To probe the influence of Nd-substitution on the crystal structure of LFO material, EXAFS analysis was performed as a powerful technique in studying the atomic locations. The fluctuating part of XAFS spectra is a result of the scattering mechanism that emitted photoelectron with a kinetic energy that allows it to travel among its nearest neighbors and scattered. The fluctuating part of spectra was extracted by the ATHENA programs and analyzed by the ARTEMIS programs which are part of the IFEFFIT Shell.[12] The EXAFS scattering data of LFO and Nd-substituted LFO cathode materials are given in Fig. 4 for comparison.

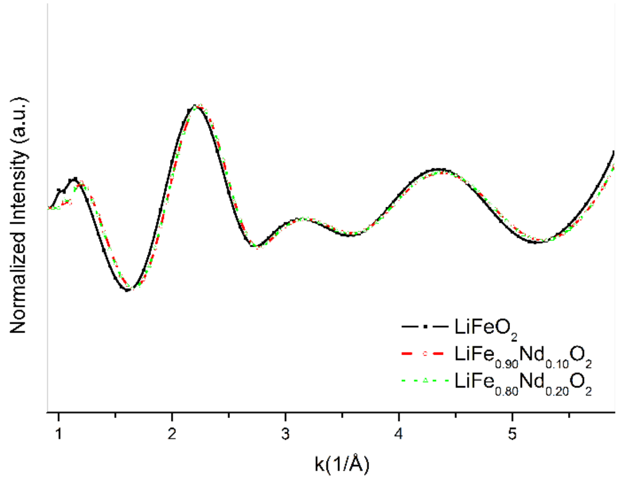

Fig. 4: Compared EXAFS spectra of the parent and Nd-substituted LFO cathode materials.

In Fig. 4, the scattering intensity of parent LFO and Nd-substituted LFO materials have an agreement in the shape of the signal envelope and with similar peak features. However, a tiny shift on the substituted LFO materials scattering data on low and high k values are due to the larger volume of the neodymium atoms which are sitting in Fe coordinations. No distortions or noise on the data were observed and this confirms the adaptation of the heavy Nd atoms in the Fe environment. The shift has a periodic structure in the data which confirms its emergence as a result of the scattered photoelectrons on the Nd atoms. The Fourier transform (FT) data of the scattering intensities are given in Fig. 5. By the results of operating a Fourier Transform (FT) on the scattering data, we can obtain the atomic displacements as atomic distances from the source Fe atom to the scattering atom on a one dimensional axis.

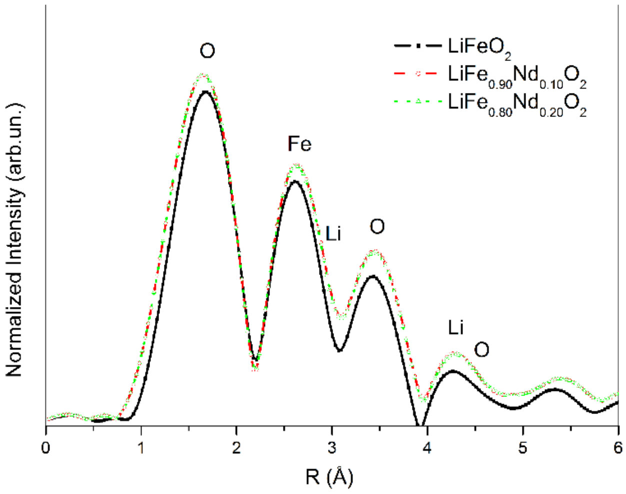

Fig. 5: Compared RDF data of the parent LFO and Nd-substituted LFO cathode materials.

In Fig. 5, normalized FT data for the parent and Nd-substituted samples are given for comparison. High agreement between the parent and Nd-substituted LFO materials confirms the stable structure against Nd-substitution. However, as seen in Fig. 4, with the Nd concentrations, the atomic peak position varied slightly and increased in intensity at some peak structures. Peaks are the signals from the overlapped atoms sitting close or at the same distance but with a different azimuthal angle. Peaks are assigned with the atomic types and where one Fe atom is sitting at the origin (0,0,0). In the Nd-substituted LFO material, no disturbance on the oxygen atoms was observed for both 10 % and 20 % Nd-substitution. In such an oxide material, O atoms interact with metal and built up strong bonds to obtain stiff molecular bands. However, in rare-earth metals, presence of the *f*-levels that avoid the rare-earths interact with oxygen directly may be the main reason for the remaining strong bonds of the Li and Fe atoms at their actual positions and intensity. According to the analysis results, the nearest neighboring atoms to the source iron atom are six O atoms at an interatomic distance of about 1.97 Å (0.197 nm, degeneracy 6). Behind O atoms, six Fe atoms were detected at a distance of about 2.890 Å (0.289 nm). In the close neighborhood of the Fe atoms, six Li atoms were located at about 2.910 Å (0.291 nm). The closest Nd atom was sitting at 2.88 Å (0.288 nm).

CONCLUSION. In this study, the electronic and crystal structure properties of the Li-ion battery cathode $LiFeO_2$ was investigated by the XAFS technique to study the influence of the *f*-electrons presence in its molecular interactions via the rare-earth Nd-substitution in the Fe coordination. The study was conducted with the XAFS calculations for the materials with the general formula of $LiFe_{1-x}Nd_xO_3$ (x: 0.00, 0.10, and 0.20). Despite the different electronic configuration of Fe and rare-earth Nd atoms, a high adaptation in Nd atoms were determined for Fe chemical environment. However, tiny energy shifts were determined on the absorption spectra of the Nd-substituted LFO materials. The reason for the shift was determined as the hybridization occurred between the *s* and *d*-levels of Fe and the *p*-level of O where Nd atoms were engaged on the *d*-levels of Fe via the *f*-levels.

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