Determination of the atomic coordinations of the substituted light atoms in materials

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Light atoms' substitution into a heavy atom coordination in materials can be a difficult process for analysis. Light atoms, which have close ionic radii with the target atom, may sit at the heavy atom's coordination. In such a case, scientist may not differ the signals from the heavy and light atom to differentiate the exact atomic coordinations of the substituted atom. As an example study, boron substitution into the chromium coordinations is studied. In the samples with boron substitution more than 10%, they became polycrystalline material where boron and chromium tended to own their own crystal structures. However, in the samples with lower substitution amounts, for x=0.05 and 0.10, boron atoms seem to sit in the Cr coordinations without any trace from boron atoms. The boron signals in the XRD patterns has not been detected, and accordingly some hypothesis put forwarded, such as; boron sat in the Cr coordinations or cause defects/impurities that can not be detected in patterns due to low amount of the light atoms. Studies were carried on a series of Li-ion battery cathode materials with the general formula $LiCr_{1-x}B_xO_2$. The analysis were performed by the x-ray absorption fine structure (XAFS) technique. As a result of the study, 10% boron substitution was determined as a treshold to protect the $LiCrO_2$ crystal structure.

1. Introduction

Scientific studies on materials confronts many problems during preparation or measurement or analysis. Ionic substitutions in a host ionic coordinations is really a big challenge where all things should be processed succesfully to yield best results in the study. To identify the electronic, chemical and crystal properties of the substituted or doped ions in the host materials needs a powerful technique to collect data which can yield exact information about the new situation of the substituted/doped element and its environment. One of the best technique that can collect data for interested studies is the XAFS (x-ray absorption fine structure) spectroscopy. The technique is element specific and sensitive to the local structure of the source atom. Other peculiarities of the techniques are its applicability to solids, liquids, gasses or mixtures, at low and high temperatures and measurable under high pressures. It also has high sensitivity to electronic or ionic states. But the best desired property is its easy measurement and analysis procedures. Mainly, XAFS is used to probe the electronic and bonding properties of elements and attracts a huge attention of the scientists due to its fruitful properties. This technique is carried out as absorption spectroscopy of the data collection process, but with a long range (tail) energy absorption to define the scattering mechanisms processed by the photoelectrons which are excited with an excess photon energy.

The data analysis of the XAFS spectra can be processed mainly in two regions. The first region is the low photon energy part of the spectra and it is called as the XANES (X-ray Absorption Near-Edge Spectroscopy) region. The second part lays just beyond the XANES part, called as the EXAFS (Extended-XAFS) region. The XANES part of the XAFS spectra contains rich information about the electronic and bonding properties of the interested atom in the materials. The spectra beyond the XANES region, which lays from the first rise below the absorption edge to approximately 80 eV beyond, is the EXAFS part. EXAFS part of the spectra is a result of the photoelectrons which are emitted from the source atom with kinetic energy. When the photoelectrons travel to a neighboring atom, outer shell electrons apply a coulombic repulsion on the photoelectron and cause a scattering. At the interaction point, incoming wavefunction of the photoelectron interfere with its outgoing wavefunctions, fluctuations occur on the spectra; positive when interference is in phase, negative when interference is out of phase. The region yields so valuable information about the crystal structure properties of materials. The EXAFS technique is also provides precious solutions to some scientific problems. Determination of the doped or substituted light elements' position in the host coordinations is one of the most confronted problem and EXAFS is the most powerful technique to solve the problem.The power of the technique comes from its tail part and analysis can yield exact data on the crystal properties of the studied material and the environment of the selected absorber atom. For the deep crystal structure analysis from the spectra, the scattering information can be extracted from the measured EXAFS spectra by using the

ATHENA and ARTEMIS softwares and processed with the background subtraction [1]. By using the softwares, the extracted scattering data can provide informations about the photoelectrons' interactions with the neighbors of the source atoms. The fourier transform of the scattering data gives us the atomic distances of the point where the scattering occured to the source atom. For the study, a new Li-ion battery cathode material with the general formula $LiCr_{1-x}B_xO_2$ is studied.

2. Results and discussion

The parent cathode material "$LiCrO_2$" is reported with trigonal rhombohedral geometry and a space group of ''$R3m$''.   In the study of Ozkendir et al., the lattice parameters of the cathode were determined as a= 2.898 A , c= 14.423 A [2]. In previous studies, the Cr-based

cathode materials were reported with the electron transfer during electrochemical reactions (Cr^{3+} to Cr^{6+}) [3]. Also, $LiCrO_2$ attracted much interest when it is a member of a polycrystalline material with its stable cycle ability and high capacity, like the Li_2MnO_3-$LiCrO_2$ material [4]. The parent oxide is not popular in the scientific studies on the battery materials due to showing poor electrochemical properties [3]. In the study of ozkendir et al, boron substitution with 5% and 10% into Cr coordinations in the $LiCrO_2$ material are reported that boron sat in the empty Cr coordinations, while 15% and 20% substitutions boron tends to form the isolated Li_2BO_4 crystal structures and formed a polycrystalline materials. The samples with 5% and 10% boron substitution, did the problem arise for the presence of the borons in Cr coordinations or not? The scattering intensity and its Fourier transform is given in Fig. 1 (a) and (b), respectively [2].
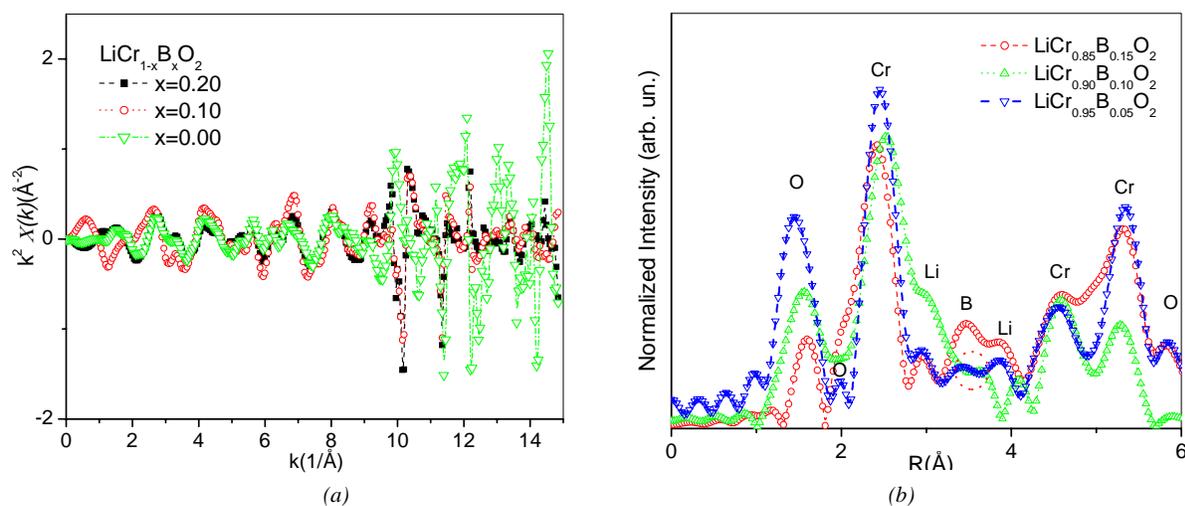

Fig. 1. (a) Scattering intensity comparison of the sample $LiCr_{1-x}B_xO_2$ for x=0.00, 0.10 and 0.20; (b) Compared RDF data of the sample $LiCr_{1-x}B_xO_2$ for x=0.05, 0.10 and 0.15

In the figure, the unsubmitted sample has the powerful scattering at high "k" values and it emphasizes close Cr neighborhood in the vicinity of the source chromium atom, i.e., short mean free path of the photoelectrons. The Fourier transform is called as the radial distribution function (RDF) and it provides us the atomic locations on a one dimensional axis, where source atom (Cr) sits at the origin. As the scattering intensities are related with the photoelectrons' interactions with the neighboring atom electrons, the RDF data can yield the exact atomic distances from the source atom. In Fig. 1 (b), the atomic types and signals from these atom groups are named with elements. As reported in the study of ozkendir et al., the boron atoms are determined for the samples 15% and 20% (where 20% is given in the figure).
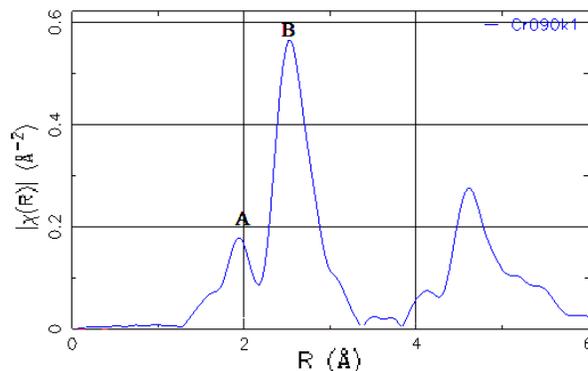

Fig. 2. Closest peaks are chosen to make the data comparison, where oxygen signals assigned with "A" and chromium signals assigned with "B"

However, no trace of boron were detected in the sample spectra for 5% and 10% boron substituted samples and hollow circle in red is placed in the figure as a guide for eyes. So, can the boron sit in Cr coordination? If yes, then there should be some changes in the compared k-powers of the strongest chromium peaks in the Fig. 1 (b). To make the comparison of the peaks with a stable peak the first two intense peaks were selected. The first closest peak to the origin, where oxygen signals are overlapped and assigned as "A" in Fig. 2 and the second powerful peak is the signals from the overlapped signals of the chromium, which is assigned as "B". The atomic masses (AM) of these elements are as; (O_8)= 15.999 g/mol and (Cr_{24}) = 52.00 g/mol. k-weight is a useful application to determine the atomic types and amounts in the RDF data.

Comparison of the change in the *k*-weight for the values $k^{n=1,2,3}$ with adjusted and normalized intensities is given in Fig. 3.
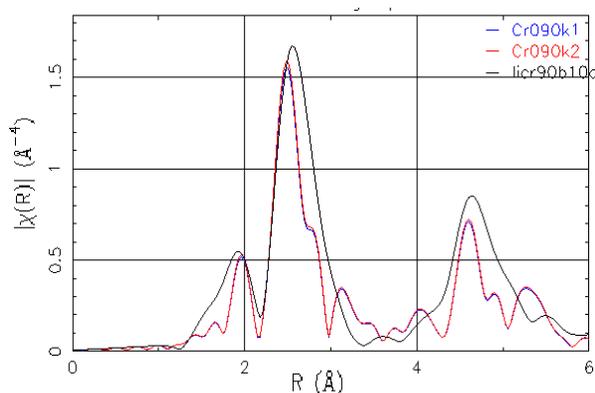

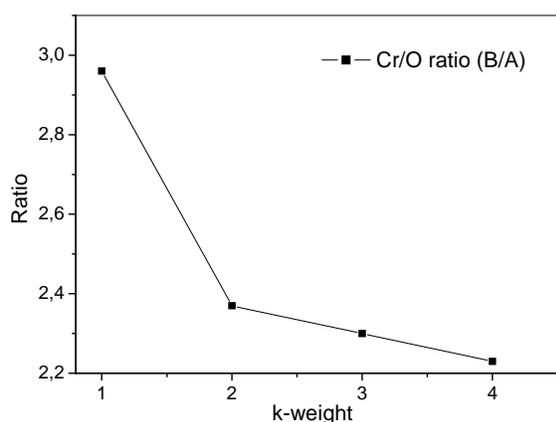*Fig. 3. Compared normalized peaks of the multiplied RDF data with n (=1,2,3) powers of k*

Fig. 4. The peak ratios " B/A" of chromium and oxygen atoms versus k weight to determine the change in average atomic weights

The normalized peaks for n=1,2 have a high agreement peak features, however, for the higher k-power multiplication (i.e., n=3), a shift at the peak location at Cr locations addresses a disturbance. Besides, similar shift is obvious on the O location peak ("A"). This phenomenon points out a small disturbance that cause shifts and just located between oxygen and chromium. So, it is clear that the lost boron atoms on the XRD peaks are actually sit into the Cr coordinations. This is also confirmed by the compared Cr/O peak intensities for "A" and "B" in Fig. 4. The ratios of the molecular weights of Cr/O for n=1 should be 3.25 for pure Cr/O.

However, for the measured data for 10% substituted material it is measured as 2.97, which means a mismatch. If the Cr coordinations are 90% occupied by the chromium (AM=52 g/mol) atoms and 10% are occupied by the boron (AM=10.811 g/mol) atom, the average atomic mass will be 47.88 (i.e., 52-(52x0.1)+ (10.811x0.1)). And the ratio with the average value of the Cr coordinations give (A/B) 2.99, which is meaningful with the measured data (in fig. 4). The unproportional decay of the normalized values of the A/B according to the powers (n=2,3) are also confirms the presence of boron in the Cr coordinations (2,37 and 2.3).

3. Conclusions

The study is focused to enlight one of the common problem for materials scientist with a solution for the readers: detection of the locations of the light atoms substituted into a heavier atom coordination. The problem to find out the exact positions and properties in its substitution processes has been addressed for many studies and it is really a hard subject. The paper focused on a problem where traces of the substituted boron atoms in the chromium coordinations in $LiCr_{1-x}B_xO_2$ cathode material with 05% and 10% substitution amounts and it was stated in the paper of ozkendir et al., where the boron signals in the XRD patterns has not been detected during the study. To solve the problem, XAFS studies were performed on the series with the general formula $LiCr_{1-x}B_xO_2$ (x=0.05, 0.10, 0.15 and 0.20). The analysis were performed by the x-ray absorption fine structure (XAFS) technique. For the study, 10% boron substitution was determined as a treshold to protect the $LiCrO_2$ crystal structure. The Fourier transform of the scattering intensities of the data were processed in two steps to identify the tarces and the exact position of boron atoms in the material. By multiplying scattering data with powers of k^n (1,2,3), the normalized data were compared and asymmetry determined as a result of the shift at the peak positions. The shifts at oxygen and chromium peaks are proved that boron atoms were sitting in the chromium locations.

References

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