

Li K-edge XANES and Li(1s) XPS Spectra of Lithium Compounds and Complexes

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Lithium is the lightest metal and used as a battery anode material [1, 2]. It is also alloyed with aluminum and magnesium for lightweight, high-performance metals for aircraft. Lithium reacts slowly with water to form a colorless solution of lithium hydroxide and molecular hydrogen and vigorously with all halogens to form halides. In four lithium halides, lithium fluoride is insoluble in aqueous solution like ones of magnesium and calcium. So some properties of lithium resemble those of other alkali metal elements, and some resemble those of alkaline-earth metal elements rather than other alkali metal elements. For a peculiar property of lithium, many researchers have extensively studied on lithium [3, 4]. However, there are no suitable analytical methods to get easily important information on the electronic states of lithium compounds and complexes. These candidates may be X-ray absorption near-edge structure(XANES) and X-ray photoelectron spectroscopy(XPS) [5-7] though they have still some difficulties, for example, X-ray source for XANES and low sensitivities for both methods.

In this study, Li K-edge XANES and Li(1s) XPS spectra of various lithium compounds and complexes have been measured to get directly the information on electronic states of lithium ions. The samples are lithium compounds with acetate, oxalate, lactate, halides, phosphate and carbonate, lithium complex, dilithium phthalocyanine, and so on. Li K-edge XANES spectra have four or five peaks in the range from 50 to 90 eV, depending on the strength of chemical bonds between lithium ions and donor atoms. Li(1s) XPS spectra also have two or three peaks in the range from 48 to 58 eV. The electron densities on lithium ions were obtained by DV-X α molecular orbital calculation [8, 9]. The relationship between these spectra and electron states will be discussed.

Chemical structures of some samples studied are shown in Fig. 1. The Li K-edge

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XANES spectra were measured by the total electron yield using BL 2 of the compact synchrotron radiation facility at Ritsumeikan University. Samples were ground to a powder in a mortar. The powder was dusted lightly onto a adhesive tape with electrical conduction on the first dynode of photomultiplier detector. The energy ranges of spectra are mainly from 50 to 90 eV. The Li(1s) XPS spectra were measured on a Ulvac-Phi ESCA-1600R spectrometer with long measuring times(ca. 5 h). X-ray source is Mg K α (1253.6 eV, 27 kV, 15 mA). The powder was also dusted lightly onto a double-backed adhesive tape with electrical conduction. To compensate charging effect, C(1s) electron line was used to be taken to be 284.8 eV.

Li K-edge XANES and Li(1s) XPS spectra of various lithium complexes can be measured under the suitable measuring conditions. A great variety of spectra have been obtained. Li K-edge XANES spectra are shown in Fig. 2. They have four or five peaks with a variety of peak intensities. The shapes and positions of their peaks may depend on the electron densities of lithium ions and covalent bond characteristics between lithium ions and donor atoms. Li(1s) XPS spectra are shown in Fig. 3. They have one peak for Li₂(ox) and lithium halides, two peaks for most lithium acylates or five peaks for only Li₂(PC) with a variety of peak intensities. The shapes and positions of their peaks may also depend on the electron densities of lithium ions and covalent bond characteristics between lithium ions and donor atoms. In this study, these spectra are classified in 4 of next each. On XANES spectra, Group A has three intense peaks in a comparatively wide energy range, and Li(sal), LiF, LiCl, LiBr, LiI and Li₃PO₄ belong to it. Group B has three intense peaks in a relatively small energy range, and only Li₂(ox) belongs to it. Group C has weak peaks, and Li(OCOCH₃), Li(lac), Li₂H₂(edta), LiOH, LiO, Li₂CO₃, Li₃N and Li₂S belong to it. Group D is similar to Group C, and only Li₂(PC) belongs to it. Also on XPS spectra, Group I has one peak, and LiF, LiCl, LiBr, LiI, LiClO₄, Li₃PO₄, Li₂(ox), and LiOSO₂CF₃ belong to it. Group II has two peaks and the peak at higher energy is stronger, and LiH₂PO₄, Li₂MoO₄, Li(OCOCH₃), Li(lac), Li(sal), Li₃(cit), Li₂H₂(edta), LiSO₄ and Li₂S belong to it. Group III has two peaks and the peak at lower energy is stronger, and LiOH and Li₃N belong to it. Group IV has three intense peaks and only Li₂(PC) belongs to it. These results were complicated. For example, Li(sal) belongs to Group A with together lithium halides on XANES spectra though to Group II with other lithium acylates on XPS spectra. A further study should be needed to get convincing interpretation for the results of these spectra. The spectra of some lithium compounds will be re-measured. All main peaks will be assigned from the results of DV-X α molecular orbital calculations. Other types of lithium complexes, such as with crown ethers, aza-crown ethers, diaza-crown ethers and so on will be prepared and their spectra will be measured.

Moreover, it became clear that chemical bond of lithium showed covalent character. This is supported from a result of DV-X α molecular orbital calculations.

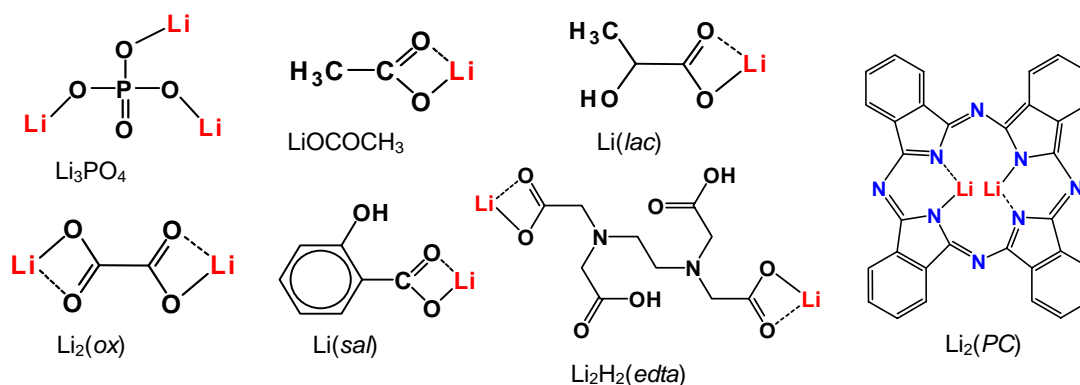


Fig. 1 Chemical structures of lithium compounds studied.

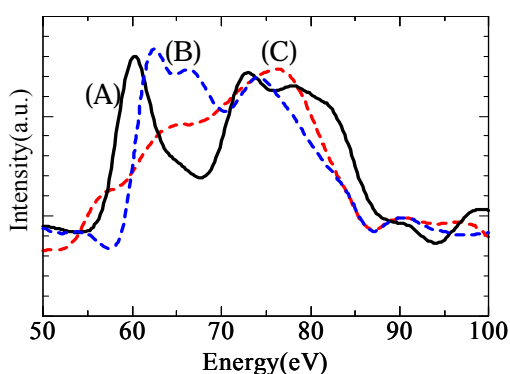


Fig. 2 Li K-edge XANES spectra of lithium compounds with (A) phosphate, (B) oxalate and (C) acetate.

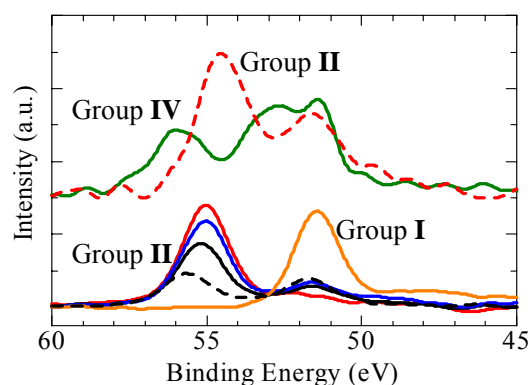


Fig. 3 Li(1s) XPS spectra of lithium compounds and complex.

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