Li K-Edge XANES Spectrochemical Analysis of Lithium Compounds

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Abstract

Successive works on extremely soft X-ray absorption spectra of lithium at Li K-edge in various compounds by means of synchrotron radiation resulted in successful finding of a way to distinguish the bonding characters of lithium in the compounds by the recognition of their spectral patterns of X-ray Absorption Near Edge Structure, XANES. During the course of the research, a spectral feature that would indicate the existence of *lithium-bonding* was found in lithium carboxylates.

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Introduction

We have been collecting Li K-edge XANES spectra of various lithium compounds, and some of the results obtained have been published elsewhere.[1-4)]

During the course of the research experiments, we have found that the spectra of lithium salts of weak organic carboxylic acids are quite different from those of strong Brőnsted acids. The core exciton peak which we believe to be associated with highly ionic lithium cation and lithium salts of strong Brönsted acids was not observed for the salts of carboxylic acids.

Although we need the theoretical background in order to elucidate the experimental results, we believe, at this moment, this must be the first experimental evidence for the existence of *lithium-bonding*. It is an analog of the *hydrogen-bonding* which characterizes the environment for hydrogen ion in carboxylic acids.

In this report we classify lithium compounds by means of the pattern recognition of the Li K-edge XANES spectrum that manifests the bonding character of lithium ion in compounds.

Experimental

Li K-edge XANES spectra were obtained by using a vacuum grating spectrometer which is available at Beam Line 2 in the SR Center of Ritsumeikan University. The BL-2 is dedicated to the studies in the extremely soft X-ray region.

Details of the instrumentation have been reported as a "STATUS OF THE BEAMLINES" in the last issue, No.9 (2007). The value of the beam current of the synchrotron ring was used as the reference signal intensity instead of directly monitoring the intensity of the incident X-ray beam at the sample. Absorption data were obtained by the total electron yield method. Electrons emitted from the sample were detected by an electron multiplier. Samples were finely ground and fixed on the surface of a first dynode of the electron multiplier by using a sheet of adhesive conductive carbon tape. All of the lithium compounds used were of analytical reagent grade and used as purchased.

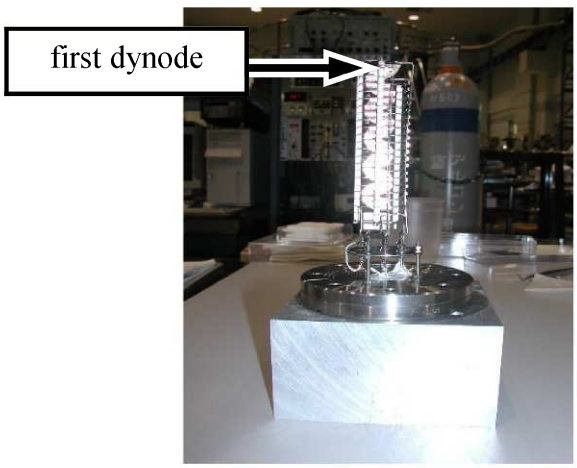

Fig. 1. Electron multiplier used for both sample holder and electron detector.

Results and Discussion

Lithium salts of strong Brönsted acids

We have already reported the Li K-edge XANES spectra of lithium halides as shown in Fig. 2, together with their theoretical interpretations by DV-Xα MO calculation.[1,2)]

Since the lithium halides are the salts of strong Brőnsted acids, one may expect that the chemical and/or physical state of the lithium ion in the salts of other strong Brönsted acids is similar to that of lithium halides. Then, the Li K-edge XANES spectra for salts of other strong Brönsted acids should be similar to those for the lithium halides.

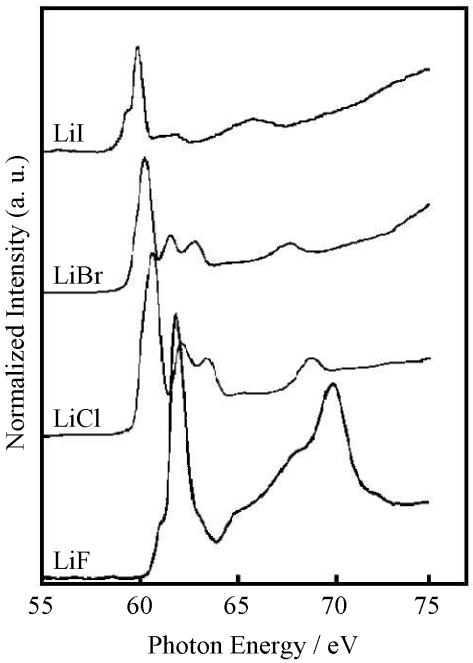

Fig. 2. Li K-edge XANES spectra of lithium salts of strong Brönsted acids: lithium halides.

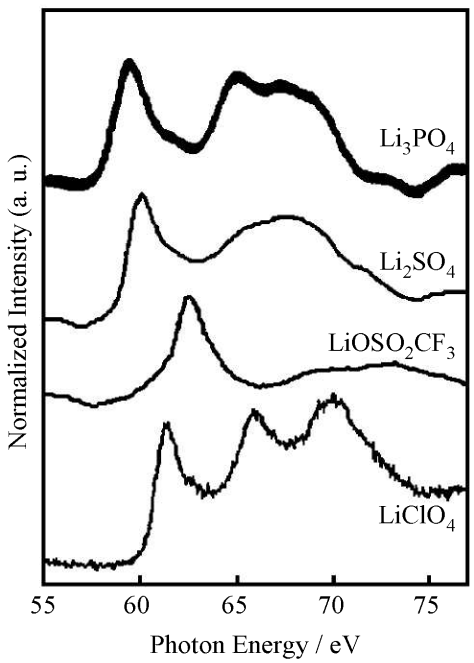

Fig. 3. Li K-edge XANES spectra of lithium salts of strong Brönsted acids: lithium salts of strong Brönsted oxoacids.

We have selected lithium salts of oxoacids as the strong Brönsted acids and obtained their Li K-edge XANES spectra. Lithium fluoride was used as a reference material for energy calibration. As indicated in Fig. 3, every spectrum for lithium salt of strong Brönsted acid has a characteristic feature, i.e. a clear peak similar to that for halides, which is due to the exciton excitation. As has been discussed in the analysis of Li K-edge XANES spectra of lithium halides, the appearance of a sharp absorption peak due to the exciton excitation indicates the lack of interaction of vacant Li 2p orbitals

with neighboring atoms. This means that the lithium atom lies on an isolated ionic state. The intensities of the peaks for the oxoacids are weaker than those for lithium halides. Different intensities and widths of the peak correspond with the different kinds of interaction between the lithium cation and its neighbor atoms or counter anion. For the lithium halides, a linear relation was observed between the energy of the peak and the electronegativity of halide anion. Such kind of correlations are not found for lithium salts of the strong Brönsted oxoacids, probably because of the lack of the consistency in the structural or electronic configuration. The spectra for lithium salts of oxoacids show rather complicated development in the higher energy region than the exciton peak. This must be also related to the character of neighboring anion interacting with the lithium ion. The strength of the corresponding acid or its dissociation constant in liquid medium seems to be related to the energy and the intensity of its exciton peak. If this is true, the Li K-edge XANES spectral pattern can be a measure for the ionicity of the bond between lithium cation-counter anion.

Lithium salts of carboxylic acids : the weak Brönsted acids — Experimental evidence for the *lithium bonding*—

Our next samples are the salts of weak Brönsted acids in order to study the electronic state of the lithium ion in the salts with counter anions having various strengths in basicity. The lithium salts of weak acids measured are some of lithium carboxylates.

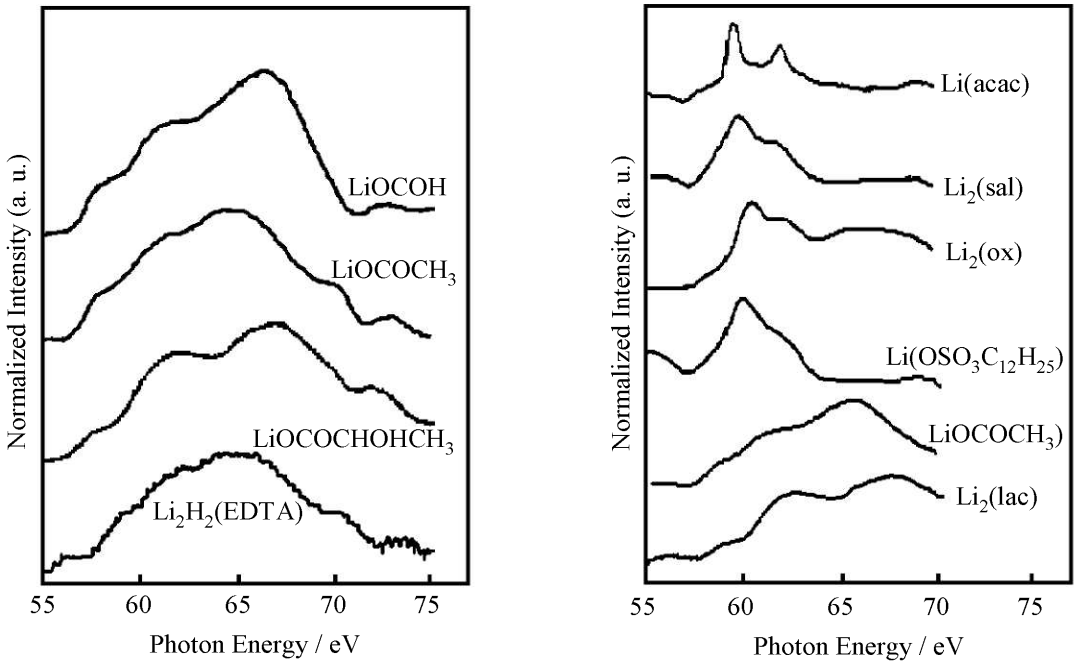

Fig. 4. Li K-edge XANES spectra of lithium salts of organic weak Brönsted carboxylic acids.

Table 1. p*K*a for various Brönsted acids in H_2O

Acid	p*K*a
H_3PO_4	2.15, 7.20, 12.4
H_2CO_3	6.35, 10.33
HCOOH	3.75
CH_3COOH	4.76
$(COOH)_2$	1.27, 4.27
o-$C_6H_4(OH)(COOH)$	2.96
$CH_3CH(OH)(COOH)$	3.66
$H_2C_4H_4O_6$(cit)	3.04
H_4(edta)	2.0, 2.67, 6.16, 10.26

Table 2. p*K*a for various Brönsted acids in acetonitrile solvent

Acid	p*K*a
$HClO_4$	2.1
$HOSO_2CF_3$	2.6
HBr	5.5
H_2SO_4	7.8, 25.9
$HOSO_2CH_3$	10.0
$(COOH)_2$	14.5, 27.7
o-$C_6H_4(OH)(COOH)$	15.2
C_6H_5COOH	20.7
CH_3COOH	22.3

As seen in Fig. 4, spectral features seem to change according to the difference in the Brönsted acid–base strength of the corresponding acid form of the salt. Dissociation constants of the acids in aqueous and organic media are listed in Tables 1 and 2, respectively. Spectra can be divided into two groups: one having a distinguishable absorption peak which could be assigned to the exciton peak, and the other having no distinguishable peak but a hilly broad band spreading over the wide range of the absorption energy from 57 to 70 eV.

In the former group, the absorption peak assigned to the exciton peak is broader in width than the corresponding peaks in the lithium salts of the strong Brönsted acids as

mentioned above and is accompanied with rather broad band at higher energy side of the maximum. On the other hand, in the latter group, the maximum in intensity is located at the highest energy side of the hilly band.

Careful estimation of the dissociation constant of each weak Brönsted acid corresponding to the respective lithium salt, leads to the conclusion that the value of the dissociation constant around $10^{-3.5}$ in the aqueous medium is the boundary condition to divide the groups.

The interesting correlation between the spectral feature and the acidity of the acid used for lithium salt allows us to use the XANES analysis as a method to find ionic lithium in various kinds of lithium salts. Our XANES study concludes that the lithium is ionic in the compounds with stronger acids, i.e. p*K*a < 3.5 in the aqueous medium.

For lithium carboxylates for which the corresponding Brönsted acids with p*K*a > 3.5, lithium atoms are not ionic if the spectroscopic criterion is followed.

Both unexpected variation in the Li K-edge XANES spectral pattern and the similarity of the profiles to those of the C K-edge XANES spectra for σ bond structure in organic compounds, may lead to the conclusion that the lithium ion is covalently coordinated to the $RCOO^-$ anion. However, considering the electronic configuration of the lithium atom, the covalent bonding should not be so strong that some ionic character in the bonding must remain: the situation is very similar to the *hydrogen-bonding*.

Although we need the theoretical work in order to elucidate the experimental results, we believe at this moment that this must be the first experimental evidence for the existence of *lithium-bonding*, specific to lithium in lithium salts of weak organic carboxylic acids, similar to the *hydrogen-bonding* in character.

Recently, Panteleev and co-workers[5)] have reported the results on the theoretical calculation on the bonding character for lithium acetates and discussed on the existence of the bridging bond of the lithium atom with the neighboring atom in the same molecule and/or in the neighboring acetate molecule. This discussion is quite in accord with the experimental results obtained by our Li K-edge XANES analysis. They have suggested the formation of a bridged circle and dimerization of lithium acetate in the solid state.

We are now carrying out DV-Xα MO calculation in order to evaluate the bond overlap population between the lithium and neighboring atoms in lithium acetate solids.

Inorganic functional lithium compounds

Lithium nitride, oxide and sulfide are well known inorganic ionic conductor materials, while lithium carbonate is known as a specific functional material useful not

only for technological purposes but also for medical ones, although the mechanism of those characteristic functions has not been cleared yet.

In order to find a way for speciation of bonding character of these compounds, we have analyzed the Li K-edge XANES spectra of some of the inorganic lithium compounds.

In all compounds including lithium carbonate and lithium hydroxide, spectral features of Li K-edge XANES do coincide in style with each other, leaving slight differences in the energy and profile of the absorption maximum in each spectrum. No distinguishable absorption maximum due to the exciton are observed but the development of three band maxima in all of the spectra.

One of the characteristic points observed in Li K-edge XANES spectra for these compounds is the extension of the boundary for the X-ray absorption edge to the lower energy side. The absorption edge locates around 54 eV for lithium sulfide, the lowest of all inorganic compounds studied, lithium oxide being the next lowest. The phenomena coincide with those for lithium salts of the organic weak Brönsted carboxylic acids, presumably because of the delocalization of the molecular orbitals, interacting with the excited electrons.

The highest energy absorption maximum for each functional inorganic compound exhibited an extensively developed spectral peak. Kowada and co-workers[6,7] have calculated bond overlap population for the cluster model of lithium sulfide super-ionic conductor by means of DV-Xα MO method. According to their results, bond overlap

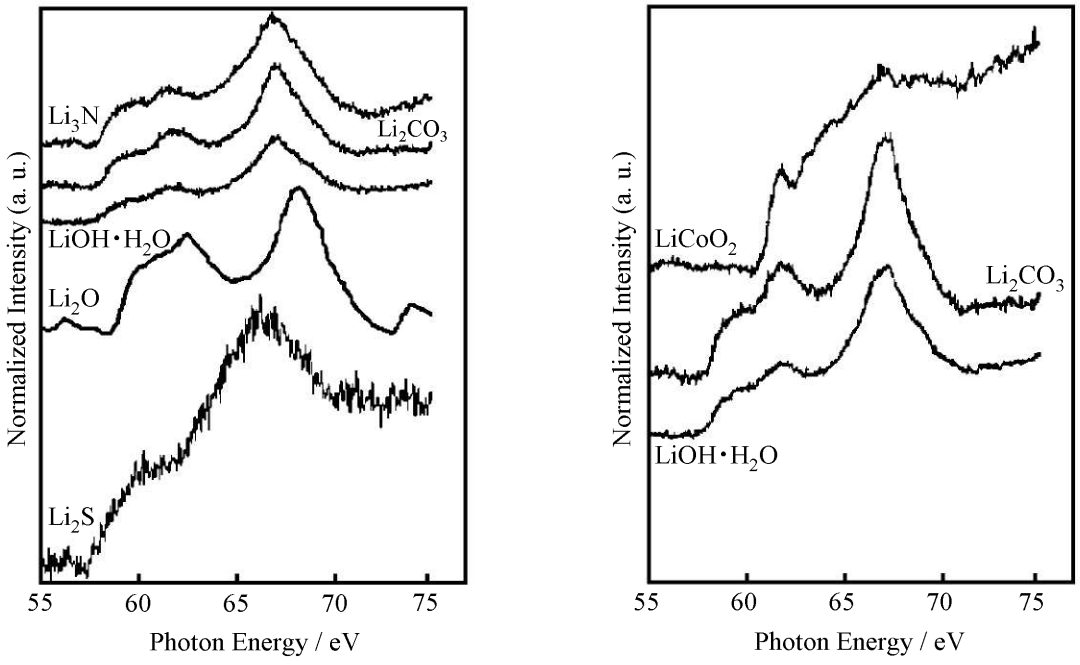

Fig. 5. Li K-edge XANES spectra of inorganic functional materials.

population between a central lithium and surrounding atoms is totally 0.7~0.8, indicating the appreciable covalent bond character between them. This must be quite helpful to interpret the extensive development of the maximum observed at the highest energy side of the XANES spectra, if this absorption maximum could be assigned to be due to the excitation of 1s electron to the σ* orbital region of the molecule concerned.

Further work should be needed to interpret the spectral pattern of Li K-edge XANES of lithium compounds.

The authors would like to stress, speculatively, the similarity in the bonding characters between the lithium salts of organic carboxylic acids and the functional inorganic lithium compounds.

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