**Li₂FeMoO₄Cl의 결정구조와 Fe 및 Mo의 전자구조 연구**

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**Electronic Structure of Iron and Molybdenum in Li₂FeMoO₄Cl and Its Crystal Symmetry**

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요 약. 전기화학적으로 리튬이온을 FeMoO₄Cl 직경내에 충전심입시킨 Li₂FeMoO₄Cl 화합물은 X-선 광전자분광 분석법로 결정화되었다. X-선 광전자분광법은 연구결과, 0<X<1 영역에서는 리튬이온의 충전심입시 Fe(III) 이온이 Fe(II) 이온으로 전환되었으며 이때 결정구조는 정방정계로 결정화되었다. 반면, 1<X<2 영역에서는 Mo(VI) 이온이 낮은 산화계로 전환되었고, 결정체 이온이나 Fe(II) 이온의 전극전 환경은 변화하지 않았다. Mo와 Fe의 3d X-선 광전자 스펙트럼은 가우스 함수로 decomvolution한 결과, Mo(VI), Mo(V) 및 Mo(IV)에 해당하는 세 종류의 피크를 분리해낼 수 있었다. 이와 같이 Mo가 원활한 상태가 상태로 존재하는 이유는 리튬이 충전심입됨에 따라 생성된 Mo(V)의 일부가 Mo(VI)와 Mo(IV)로 disproportionation되기 때문이다.

ABSTRACT. Lithium intercalates, Li₂FeMoO₄Cl (1<X<2) prepared by electrochemical lithiation of FeMoO₄Cl, crystallizes in monoclinic structure for all x values as revealed by x-ray diffraction and galvanostatic discharge experiments. According to the x-ray photoelectron spectroscopic study, Fe(III) is at first reduced to Fe(II) upon lithium intercalation with the x domain of 0<X<1, where the crystal symmetry is changed from tetragonal to monoclinic. On the other hand, Mo(VI) is reduced to lower valent state upon further lithium intercalation (1<X<2), where no crystal symmetry transformation and reduction of Fe(II) to lower valent state are observed. The Mo 3d spectrum for Li₂FeMoO₄Cl appears as a complex shape, but can be deconvoluted into the three sets of the doublet on the basis of Gaussian function, whose three sets correspond to Mo(VI), Mo(V) and Mo(IV) states, respectively. The mixed valent states of molybdenum after further lithiation may be due to a competitive reaction between the formation of Mo(V) and its disproportionation to Mo(IV) and Mo(VI).
The pristine material, FeMoO$_4$Cl, has vacant octahedral sites in the interlayer space composed of four oxygen and two chlorine atoms (Fig. 1) and two reducible cations such as Fe(III) and Mo(VI) within the sheet. According to our previous crystal structure study on LiFeMoO$_4$Cl, we have found that two of the four vacant octahedral sites are occupied by lithium ions. It is therefore expected that the two more Li$^+$ ions could be intercalated into the two remaining vacant sites of the interlayer of LiFeMoO$_4$Cl without any reconstruction of its crystal structure.

In this report, an attempt was made to synthesize a further lithiated phase Li$_x$FeMoO$_4$Cl ($x \geq 2$) and X-ray photoelectron spectroscopic study has been carried out to understand the evolution of electronic structure of transition elements upon lithium intercalation.

EXPERIMENTAL

FeMoO$_4$Cl has been prepared in the same manner as described previously. The mixture of Fe$_2$O$_3$, MoO$_3$ and FeCl$_3$ (molar ratio 1:3:1.05) was heated in a sealed Pyrex tube at about 380 °C for several days according to the chemical vapor transport (CVT) technique. Electrochemical lithiation has been carried out with a two-electrode cell of the form:

$$\text{Li/LiClO}_4 \text{ in PC/FeMoO}_4\text{Cl + ketjen black,}$$

The cathode consists of finely ground FeMoO$_4$Cl mixed with ketjen black (up to 30% by weight) to enhance the electronic conductivity. LiClO$_4$ solution (1M) in propylene carbonate (PC) absorbed in glass-wool disc was used as the liquid electrolyte. Cell was galvanostatically discharged and charged at constant current densities of 30−100 μA/cm$^2$ under argon atmosphere.

X-ray powder diffraction data have been obtained by multi channel analyzer where Cu-Kα (λ = 1.5405 Å) was used. X-ray photoelectron spectra using a Mg-Kα radiation (1253.6 eV) have been recorded on an ESCALAB/200R V.G. Scientific X-ray Photoelectron Spectrometer equipped with Micro-PDP 11/53 computer system. The base pressure was maintained in the $\sim 10^{-6}$ torr throughout all operation. Instrumental work function was calibrated by the Au (4f$_{7/2}$) binding energy at 83.8 eV. The powder sample was pressed into pellet, mounted on the sample holder which was covered with a gold sheet and put into the chamber without exposure to air. All binding energies were corrected with the carbon 1s line (284.4 eV).

RESULTS AND DISCUSSION

The electrochemical lithium intercalation-deintercalation has been realized either by continuous discharge-charge under constant current density as shown in Fig. 2. The curve shape in the domain between FeMoO$_4$Cl and LiFeMoO$_4$Cl is completely
reversible, and the small voltage difference indicates a reduced polarization. Though an effort has been made to perform the discharge-charge experiment in the x domain of 0≤X≤2 by the open circuit voltage method, the open circuit voltage diagram could not be obtained due to the large polarization effect in the x domain of 1≤X≤2. The constant potential of discharge curve for x>1 underlines the formation of the two phases without any structural transformation, and which is in turn confirmed by the XRD analysis as shown in Fig. 3.

The structure of a further lithiated phase with nominal composition Li₂FeMoO₄Cl is similar to that of LiFeMoO₄Cl and closely related to that of FeMoO₄Cl. According to the powder X-ray diffraction pattern (Fig. 3(c)), the crystal symmetry of Li₂FeMoO₄Cl is found to be monoclinic with lattice parameters a = 7.042(2), b = 6.906(1), c = 5.049(1) Å and β = 91.37°. The indexed XRD pattern for Li₂FeMoO₄Cl is given in Table 1. Even two moles of lithium are intercalated, the crystallinity is still retained, which might be due to the fact that the vacant octahedral sites in the lattice allowed are exactly consistent with four Li⁺ ions per FeMoO₄Cl unit cell (z=2), as shown in Fig. 1.

In order to investigate whether the distribution of lithium ions has an influence on the X-ray intensity or not, the theoretical X-ray diffraction intensity for two lithiated phases LiFeMoO₄Cl and Li₂FeMoO₄Cl has been calculated. On the basis of monoclinic unit cell of LiFeMoO₄Cl with space group P2₁/m determined by X-ray and neutron powder diffraction data, lithium ions in LiFeMoO₄Cl and Li₂FeMoO₄Cl (z=2) are placed in the two crystallographic interlayer octahedral sites at (0.26, 0.25, 0.25) and (0.77, 0.75, 0.25), and those of Li₂FeMoO₄Cl (z=2) are placed at (0.26, 0.25, 0.25), (0.26, 0.75, 0.25), (0.77, 0.75, 0.25) and (0.77, 0.25, 0.25), where iron ions occupy the eight corners of the cell and one more occupies the center of the cell. As expected, the calculated X-ray intensity patterns between LiFeMoO₄Cl and Li₂FeMoO₄Cl cannot be distinguished even though lithium ions occupy all the octahedral sites remained in the LiFeMoO₄Cl lattice, which is surely due to the small values of the atomic scattering factor of lithium ion.

The (00l) peaks of the lithiated phase are shifted to the higher angle than those of the pristine FeMoO₄Cl, which indicates a strong electrostatic
reversible, and the small voltage difference indicates a reduced polarization. Though an effort has been made to perform the discharge-charge experiment in the $x$ domain of $0 \leq X \leq 2$ by the open circuit voltage method, the open circuit voltage diagram could not be obtained due to the large polarization effect in the $x$ domain of $1 \leq X \leq 2$. The constant potential of discharge curve for $x > 1$ underlines the formation of the two phases without any structural transformation, and which is in turn confirmed by the XRD analysis as shown in Fig. 3.

The structure of a further lithiated phase with nominal composition $Li_xFeMoO_4Cl$ is similar to that of $LiFeMoO_4Cl$ and closely related to that of FeMoO$_4Cl$. According to the powder X-ray diffraction pattern (Fig. 3(c)), the crystal symmetry of $LiFeMoO_4Cl$ is found to be monoclinic with lattice parameters $a = 7.042(2)$, $b = 6.906(1)$, $c = 5.049(1)\,\text{Å}$ and $\beta = 91.37^\circ$. The indexed XRD pattern for $LiFeMoO_4Cl$ is given in Table 1. Even two moles of lithium are intercalated, the crystallinity is still retained, which might be due to the fact that the vacant octahedral sites in the lattice allowed are exactly consistent with four Li$^+$ ions per FeMoO$_4Cl$ unit cell (z=2), as shown in Fig. 1.

In order to investigate whether the distribution of lithium ions has an influence on the X-ray intensity or not, the theoretical X-ray diffraction intensity for two lithiated phases $LiFeMoO_4Cl$ and $Li_xFeMoO_4Cl$ has been calculated. On the basis of monoclinic unit cell of $LiFeMoO_4Cl$ with space group $P2_1/m$ determined by X-ray$^1$ and neutron powder diffraction data$^2$, $Li$ ions in $LiFeMoO_4Cl$ ($z=2$) are placed in the two crystallographic interlayer octahedral sites at $(0.26, 0.25, 0.25)$ and $(0.77, 0.75, 0.25)$, and those of $Li_xFeMoO_4Cl$ ($z=2$) are placed at $(0.26, 0.25, 0.25)$, $(2.0, 0.75, 0.25)$, $(0.77, 0.75, 0.25)$, and $(0.77, 0.25, 0.25)$, where iron ions occupy the eight corners of the cell and one more occupies the center of the cell. As expected, the calculated X-ray intensity patterns between $LiFeMoO_4Cl$ and $Li_xFeMoO_4Cl$ can not be distinguished even though lithium ions occupy all the octahedral sites remained in the $LiFeMoO_4Cl$ lattice, which is surely due to the small values of the atomic scattering factor of lithium ion.

The (000) peaks of the lithiated phase are shifted to the higher angle than those of the pristine FeMoO$_4Cl$, which indicates a strong electrostatic...
no change in the XPS lines for 0 1s and Cl 2p except for Fe 2p and Mo 3d before and after lithiation. In the case of LiFeMoO$_4$, only the BE's of Fe 2p core lines were changed due to the reduction of Fe(III) to Fe(II), whereas the noticeable change in Li$_2$FeMoO$_4$Cl occurs in Mo 3d core lines as well as Fe 2p core lines. The changes in the BE of Fe 2p core lines for Li$_2$FeMoO$_4$Cl are shown in Fig. 4(c). The BE's of Fe 2p$_{3/2}$ and 2p$_{1/2}$ core electrons for FeMoO$_4$Cl are estimated as 724.3 eV and 711.0 eV, respectively, whereas those of Fe 2p core lines for Li$_2$FeMoO$_4$Cl are shifted to lower binding energy by ~1 eV as those for LiFeMoO$_4$Cl, which indicates a decrease in the oxidation state of iron (Fe(III) → Fe(II)).

It is found that 2p XPS spectra of the compounds containing 3d-group transition metals (Fe, Co, Ni, Cu, etc.) are particularly difficult to analyze because of a steeply rising background and broadening line widths caused by multiplet splitting and shake-up phenomena. Multiplet splitting of core-level peaks can occur when the system has unpaired electrons in the valence levels. And this effect causes broadening (with asymmetry) in both 2p$_{3/2}$ and 2p$_{1/2}$ peaks. The multiple electron transitions producing shake-up process are now similarly well understood. Very strong shake-up satellites are observed for certain transition metal and rare earth compounds which have unpaired electrons in 3d or 4f shells, respectively.

Fe 2p spectra, as in Fig. 4, show the parent doublet peaks, which are broadened (ca. 3.3 eV) with satellites. When applying the above considerations to the present system, it can be deduced that Fe(III) ion in FeMoO$_4$Cl and Fe(II) in Li$_2$FeMoO$_4$Cl ($x=1, 2$) are in high spin ($^3$S) and ($^3$D) states with 5 and 4 unpaired valence electrons, respectively. The BE's for Fe 2p$_{3/2}$ and 2p$_{1/2}$ are plotted with respect to the oxidation states of iron for various iron-containing compounds along with FeMoO$_4$Cl and its lithium derivatives (Fig. 5). As expected, an increase in oxidation state provides an increase in binding energy. And it is found that the Fe 2p BE's of 723.7 eV (Fe 2p$_{3/2}$) and 710.4 eV (Fe 2p$_{1/2}$) in Li$_2$FeMoO$_4$Cl corresponds to the Fe(II) state. At first, it is thought that Mo(VI) in the lattice might be reduced to Mo(V), since no XPS evidence of reduction from Fe(II) to Fe(0) in Li$_2$FeMoO$_4$Cl was observed upon further lithiation.

Fig. 4. Fe 2p XPS spectra of (a) FeMoO$_4$. (b) LiFeMoO$_4$Cl and (c) Li$_2$FeMoO$_4$Cl after Ar ion sputtering for several min. Satellite peaks are indicated by arrows.
Mo 3d spectra for both FeMoO$_4$Cl and LiFeMoO$_4$Cl show the same shape (full width at half maximum (FWHM) = 1.6 eV for FeMoO$_4$Cl and LiFeMoO$_4$Cl) with no satellite lines except x-ray satellites 8 eV lower than the main XPS lines and BE's indicating that Mo(VI) species is not reduced even after 1 mol of lithium intercalation. On the other hand, the Mo 3d spectrum for LiFeMoO$_4$Cl (Fig. 6(c)) is rather complex in shape due to the superimposed doublets of several oxidation states. In the curve fitting procedure, a linear background is assumed and the line shape is derived from the analysis of the Mo(VI) doublet in the FeMoO$_4$Cl spectrum. The doublet was well reproduced by Gaussian lines. The FWHM used in the fitting is by 25% higher than that of the Mo 3d line for FeMoO$_4$Cl spectrum (1.6 eV). The intensity between Mo 3d, lines ($j=3/2$ and 5/2) for FeMoO$_4$Cl is observed clearly in the ratio of 2 : 3, which is consistent with the expected intensity of the doublet peaks given by the ratio of their respective degeneracy ($2j+1$).

The BE's and the fitting parameters are listed in Table 4. The best computer fit for the Mo 3d envelope is shown in Fig. 6(c), and the spectrum could be deconvoluted into three sets of the doublet. The BE's of Mo 3d$_{3/2}$ and 3d$_{5/2}$ electrons vs. the oxidation states are also plotted for various molybdenum containing compounds with different oxidation states (Fig. 7). As in the iron case the BE's of Mo 3d electrons increase as the oxidation state become more positive. The BE value for molybdenum found in Li$_2$FeMoO$_4$Cl are nearly consistent with those for other Mo(VI), Mo(V) and Mo(IV) species such as MoO$_3$, Na$_2$MoO$_4$·2H$_2$O, Al$_2$.
(MoO₄)₃ and CoMoO₄ for Mo(VI), Mo₂O₇ for Mo(V), and MoO₂ for Mo(IV), respectively. In addition, a slight broadening of O 1s peak for LiFeMoO₄Cl is observed, which underlines that the oxygen ions in this compound are in different chemical environments one another due to the presence of mixed oxidation states of molybdenum in the lattice.

The amounts of Mo(VI), Mo(V) and Mo(IV) present in the LiFeMoO₄Cl lattice could be quantitatively estimated from the intensities of the corresponding deconvoluted spectrum and are approximately the same for one another. It is therefore concluded that Mo(VI) is reduced to thermodynamically unstable Mo(V) upon two moles of lithium intercalation, but there are two possible causes for the presence of Mo(VI) and Mo(IV); 1) disproportionation of Mo(V) producing Mo(VI) and Mo(IV), and 2) the concentration gradient during lithium intercalation. In the latter case, it can be expected that the sample surface is probably enriched with Mo(IV) contents and the bulk with Mo(VI) ones. In the Mo 3d spectrum of LiFeMoO₄Cl before Ar ion sputtering, BE's are corresponding to Mo(VI) state, which is thought to result from reoxidation of Mo(V) or Mo(IV) at the pellet surface. On the other hand, there is no variation in the complex shape of Mo 3d spectra after 3 and 5 min. of Ar ion sputtering (a depth of 3 Å from the surface is etched by Ar ion sputtering).

Therefore, the two species, Mo(VI) and Mo(IV), could be considered as a result of the disproportionation of Mo(V). The emf of Mo species can be built up as follows:¹⁴

\[
\begin{align*}
+0.41 & \quad +0.73 \\
\text{Mo(VI)} & \rightarrow \text{Mo(V)} & \rightarrow \text{Mo(IV)} \\
+0.57 & \end{align*}
\]

It is not surprising that the pentavalent molybdenum ion is thermodynamically unstable with respect to disproportionation. Thus, upon further lithium intercalation, Mo(VI) in the lattice of LiFeMoO₄Cl is previously reduced to Mo(V) instead of the reduction of iron (Fe(II) → Fe(0)); electrode potential = −0.41 V). But, as mentioned above, the reduced Mo(V) ions undergo disproportionation to Mo(VI) and Mo(IV). The reason why the Mo(V) species coexist with Mo(VI) and Mo(IV) ones might be due to the fact that the formation of Mo(V) and its disproportionation reaction are in competition.

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REFERENCES