Lithium Insertion to Iron-substituted Molybdenum Trioxide

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Changes in the lithium insertion characteristics by introducing the inhomogeneity to α -MoO₃ having a van der Waals layer gap were investigated. The partially iron-substituted α -MoO₃ was prepared by the solid state reaction of α -MoO₃ and Fe₂O₃ powders. X-ray diffraction and infrared spectroscopic results showed that a solid solution of iron-substituted α -MoO₃, having the same lattice structure and bonding state as α -MoO₃, existed up to an atomic fraction of Fe/(Mo+Fe)=ca.0.1. After chemical lithiation of both α -MoO₃ and iron-substituted α -MoO₃, a discontinuous change of the interlayer distance was observed at around the composition of x (=Li/Mo or Li/(Mo+Fe))=ca.0.2. At $x>0.2$, a larger interlayer expansion in iron-substituted α -MoO₃ than in α -MoO₃ occurred probably due to the difference in van der Waals force. By substituting Mo with Fe in α -MoO₃, the open-circuit potential became higher and the discharge capacity increased considerably at the same time.

1 INTRODUCTION

As a possible cathode material for lithium secondary cells which are expected as a high energy density power source for many portable electronic apparatus or as a load levelling battery, various transition metal chalcogenides with van der Waals layer gap were so far examined. However, they are easily suffered from irreversible lattice change upon lithium insertion because the layers are bound weakly. In order to avoid the irreversible lattice change and to improve the charge-discharge cycling efficiency, much attempts have been proposed¹⁾ to substitute with foreign transition metal or to introduce ionic character to the interlayer bonding.

Orthorhombic molybdenum trioxide, α -MoO₃, with layered lattice structure has attracted much attention as a possible intercalation cathode material for a lithium secondary cell and lithium insertion to this oxide has been investigated by many researchers. Besenhard *et al.*²⁾ discussed that structural and transport properties of lithiated MoO₃ showed the correlation between the lattice expansion and the chemical diffusion coefficient of lithium. On the other hand, amorphous MoO₃ has a larger capacity and better reversibility in charge-discharge cycling as compared with crystalline MoO₃³⁾. Among these approaches, Julien *et al.*⁴⁾ suggested that oxygen vacancies introduced upon the preparation of MoO₃ films affected lithium insertion reaction.

In this work, as an attempt to improve the characteristics of MoO₃ as an insertion host having van der Waals gap, Mo was partially substituted with Fe and the chemical lithiation of iron-substituted α -MoO₃ was investigated comparatively with that of α -MoO₃.

2 EXPERIMENTAL

2.1 Preparation of iron-substituted α -MoO₃

Iron-substituted α -MoO₃ was prepared by the solid state reaction of α -MoO₃ (Soekawa 99.9%) and Fe₂O₃ (Kanto-Kagaku, 99.0%). The mixture was heated at 500°C in air for 120 hours in a platinum crucible and then quenched. α -MoO₃ powders as a reference material was also treated by the same method.

2.2 Chemical lithium insertion

Chemical lithiation was carried out by using a butyllithium (*n*-BuLi) (Kanto Kagaku, 1.6 mol·dm⁻³ solution in hexane) as a reducing agent. Both iron-substituted α -MoO₃ and α -MoO₃ powders were lithiated by 0.06 mol·dm⁻³ *n*-BuLi/hexane solution at room temperature for 1-170 hour in a glass tube filled with N₂ gas. The extent of chemical lithiation, x =Li/(Mo+Fe) or Li/Mo, was determined by atomic absorption analysis for Li, where lithiated samples were dissolved in hot concentrated sulfuric acid and then diluted with distilled water.

2.3 Analytical procedures

Powder X-ray diffraction (XRD) patterns were obtained using Rigaku diffractometer (Rad=C or Rint-1300) with a monochromatized FeK α radiation (λ =1.9357Å) in the presence of the inner standard of an Si powder.

Infrared (IR) spectra were obtained at room temperature within a range of 400-1200 cm⁻¹ with a KBr disk method using an FT-IR spectrometer (Bio-Rad, FTS-65), where all samples were dried *in vacuo* for 1 hour just before the measurement.

Any changes in XRD patterns and IR spectra of lithiated samples during the analyses were not observed.

2.4 Electrochemical measurements

Sample electrode disks of 5 mm in diameter and 20-30 mg in weight were made from a mixture of 80% active material, 10% acetylene black and 10% poly(tetrafluoroethylene) (PTFE). The mixture was pressed onto a Ni-mesh at a pressure of 2×10^6 Pa for 2 min and the Ni-mesh was connected to a copper wire with silver paste. The edge and the back faces were cov-

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Fig. 1 Typical powder XRD patterns of (A) α - MoO_3 and (B) $\text{Fe}_\gamma\text{Mo}_{1-\gamma}\text{O}_3$ ($\gamma=0.1$).

Fig. 2 Changes in the relative intensity of typical XRD peaks with γ .

1: $I_{(020)}$, 2: $I_{(200)}$, 3: $I_{(002)}$

ered with silicon rubber. A beaker type cell was constructed in a dry box, where an Li counter electrode, another Li reference electrode and a $1 \text{ mol} \cdot \text{dm}^{-3}$ LiClO_4 /propylene carbonate (PC) electrolyte solution were employed at 25°C .

3 RESULTS AND DISCUSSION

3.1 Crystal structure and bonding state of iron-substituted α - MoO_3

Typical powder XRD pattern of $\text{Fe}_\gamma\text{Mo}_{1-\gamma}\text{O}_3$ ($\gamma=0.1$)

Fig. 3 (A) Lattice structure of α - MoO_3 and (B) $\nu(\text{Mo-O})$ IR absorption bands.

is compared with that of α - MoO_3 mother in Fig. 1. The original XRD pattern of α - MoO_3 is maintained and any new diffraction peak is not found at $\gamma < 0.1$, whereas several peaks attributable to Fe_2O_3 or $\text{Fe}_2(\text{MoO}_4)_3$ appear at $0.1 < \gamma$. These results show that the substitution of Mo with Fe occurs without changing a mother lattice of α - MoO_3 within a composition range of $0 \leq \gamma \leq 0.1$, where the lattice parameters remain almost constant (within 0.1%). The relative intensity of an (hkl) peak of the iron-substituted sample to that of α - MoO_3 mother, on the other hand, decreases with increasing γ as can be seen in Fig. 2. Especially, the (020) peak becomes weaker remarkably with increasing γ suggesting that the lamellar structure is disordered by replacing Mo with Fe. When we consider the valence of these cations, the oxygen vacancy should be introduced because Mo(VI) ions are substituted with Fe(III). Accordingly, iron-substituted samples should be designated as $\text{Fe}_\gamma\text{Mo}_{1-\gamma}\text{O}_{3-\delta}$ where $\delta = (3/2)\gamma$.

Less steep change in relative intensity with γ at $x > 0.05$ may be a result of additional formation of vacancy at another sites than O_1 , but detailed analysis must be necessary (see also Fig. 4).

Fig. 4 A change in the relative IR absorption intensity of $A_{\text{Mo-O1}}/A_{\text{Mo-O3}}$ with y .

The crystal structure and IR spectrum of $\alpha\text{-MoO}_3$ are given in Fig. 3, where two absorption bands at around 1000 and 870 cm^{-1} are assigned to $\nu(\text{Mo-O}_1)$ and $\nu(\text{Mo-O}_3)$ stretching modes, respectively⁶⁾. Most absorption bands for iron-substituted sample are almost identical to those for $\alpha\text{-MoO}_3$. As seen in Fig. 4, however, the relative absorbance of $A_{\text{Mo-O1}}/A_{\text{Mo-O3}}$ decreases with increasing y , suggesting that the concentration of oxygen facing to van der Waals gap (O_1) decreases with increasing y and therefore that the oxygen vacancy is introduced preferentially at O_1 sites at least up to $y=0.05$. Therefore, iron substituted $\text{Fe}_y\text{Mo}_{1-y}\text{O}_3$ with $y=0.05$ is used as an host material for lithium insertion.

3.2 Lithiation of $\alpha\text{-MoO}_3$ and $\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$

Figure 5 shows the open-circuit potential of chemically lithiated samples as a function of x . For $\alpha\text{-MoO}_3$ the open-circuit potential lowers gradually with increasing x showing a small hump at about $x=0.2$, while for $\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$ the potential plateau at 3.35 V lies in a region of $0.2 < x < 0.5$ and the potential drops sharply at $x=0.5$. Changes in these dependencies at about $x=0.2$ will be related with the fact that structural changes occur at about $x=0.2$, as mentioned below (see Fig. 8). Hence, the chemical potential of lithium is different in these two host materials, probably because the coordination state of Li^+ ion in $\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$ differs from that in $\alpha\text{-MoO}_3$. Since x value corresponding to the plateau region is considerably larger than y value, substituting Fe ions are hardly considered to affect the coordination of Li^+ ions directly.

The analogous potential difference between $\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$ and $\alpha\text{-MoO}_3$ host materials can be found out during galvanostatic discharge at 0.1 $\text{mA}\cdot\text{cm}^{-2}$ as shown in Fig. 6. Iron-substituted samples have a characteristic

Fig. 5 The open-circuit potentials of chemically lithiated Li_xMoO_3 (O) and $\text{Li}_x\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$ (Δ) ($y=0.05$).

Fig. 6 Galvanostatic discharge curves at 0.1 $\text{mA}\cdot\text{cm}^{-2}$
1: $y=0$ ($\alpha\text{-MoO}_3$), 2: $y=0.05$, 3: $y=0.10$.

potential plateau and much discharge capacity than $\alpha\text{-MoO}_3$ at the same time. Curve 1 in this figure is in good agreement with a reported⁴⁾ data for $\alpha\text{-MoO}_3$.

As reported by Besenhard *et al.*³⁾, the crystallinity of $\alpha\text{-MoO}_3$ is lowered by electrochemical or chemical lithiation owing to the weak bonding across van der Waals layer gap. In the present work, considerable intensity decrease and broadening of XRD peaks are observed, and some XRD peaks corresponding to different interlayer distances appear at the same time. Chemically lithiated samples were heat-treated at 150°C *in vacuo* for 1 hour in order to investigate the stable phases in more detail.

As can be seen in Fig. 7, only a few XRD peaks re-

Fig. 7 Powder XRD patterns of (A) α - MoO_3 and (B) chemically prepared $\text{Li}_{0.3}\text{MoO}_3$.

Fig. 8 The interlayer distance of $d_{(020)}$ after chemical lithiation of α - MoO_3 (O) and $\text{Fe}_{0.9}\text{Mo}_{1-y}\text{O}_{3-\delta}$ (Δ) ($y=0.05$).

main after heat-treatment of lithiated samples. When the lines at around $2\theta=10^\circ$ are assumed as (020) reflections from respective new phases, their (040) and (060) family lines can be found out at a higher 2θ region. Thus, several phases having different basal spacings are considered to be formed upon chemical lithiation.

The interlayer distance and the intensity of these

Fig. 9 The intensity of XRD peaks from chemically lithiated (A) α - MoO_3 and (B) $\text{Fe}_{0.9}\text{Mo}_{1-y}\text{O}_{3-\delta}$ ($y=0.05$).

1: $d \approx 6.9 \text{ \AA}$, 2: $d \approx 7.8 \text{ \AA}$, 3: $d \approx 9.4 \text{ \AA}$

(020) XRD lines are shown in Fig. 8 and Fig. 9, respectively, as functions of x . Within a range of $0 < x < 0.2$, lithiated α - MoO_3 is a single phase solid solution whose $d_{(020)}$ is almost independent of x . $I_{(020)}$, however, decreases remarkably with increasing x and this fact may correspond to the continuous lowering of the open-circuit potential in this range of x . Similar results are obtained for lithiated $\text{Fe}_{0.9}\text{Mo}_{1-y}\text{O}_{3-\delta}$ and the original interlayer distance of α - MoO_3 ($\approx 6.9 \text{ \AA}$) does not change at $0 < x < 0.2$. It is probable that inserted Li^+ ions are accommodated in the intralayer site at $0 < x < 0.2$ as is the case for proton insertion⁷⁾.

At $x > 0.2$, a new phase having the interlayer gap of $\approx 7.8 \text{ \AA}$ appears discontinuously for an α - MoO_3 host. Li^+ ions are inserted probably into this wider interlayer gap than original one. Similar expansion of interlayer gap was reported by Besenhard *et al.*³⁾ and Dmitrienko *et al.*⁸⁾, although they regarded the expansion as continuous. It is plausible from the present XRD data that discontinuous changes in the interlayer gap due to lithiation take place in case of α - MoO_3 .

On the other hand, for $\text{Fe}_{0.9}\text{Mo}_{1-y}\text{O}_{3-\delta}$, another phase with interlayer gap of $\approx 9.5 \text{ \AA}$ forms mainly at $0.2 < x < 0.5$ and Li^+ ions are expected to be inserted to this gap. The difference of the second phase preferentially formed by lithiation at $0.2 < x < 0.5$ might be due to the different oxygen coordination of Li^+ ions in the interlayer gap. It is probable that the difference is re-

Fig. 10 IR spectra of (A) Li_xMoO_3 and $\text{Li}_x\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$ ($y=0.05$).

(A) 1: $x=0$ 2: $x=0.15$ 3: $x=0.21$ 4: $x=0.38$.
 (B) 5: $x=0$ 6: $x=0.13$ 7: $x=0.21$ 8: $x=0.38$.

lated to the concentration of oxygen vacancy facing to the interlayer gap. The larger (020) expansion at $0.2 < x < 0.5$ may arise from the weaker van der Waals force owing to the existence of oxygen vacancies, and more flat open-circuit potential will be caused by an apparent strain-mediated attractive interaction between guest ions in the interlayer channels⁹⁾.

IR spectra of lithiated $\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$ and $\alpha\text{-MoO}_3$ are

in Fig. 10(A) and (B), respectively. In both cases, $\nu(\text{Mo-O}_1)$ and $\nu(\text{Mo-O}_3)$ peaks do not shift substantially at $0 < x < 0.2$, though $A_{(\text{Mo-O}_3)}$ decrease preferentially with increasing x , suggesting that inserted Li^+ ions probably interact not with O_1 facing to van der Waals gap but mainly with O_3 . At $0.2 < x$, on the other hand, $A_{(\text{Mo-O}_1)}$ decreases characteristically and new absorption bands appear at a smaller wavenumber region than original $\nu(\text{Mo-O}_1)$. The fact that the slight shift of $\nu(\text{Mo-O}_1)$ to a larger wavenumber is observed only for $\alpha\text{-MoO}_3$ implies that the effect of inserted Li^+ ions is stronger in $\alpha\text{-MoO}_3$ than in $\text{Fe}_y\text{Mo}_{1-y}\text{O}_{3-\delta}$.

The appearance of new IR absorption bands should correspond to the formation of new phases detected by XRD measurements. Detail analyses of the lattice position of inserted Li^+ ions, the concentration of oxygen vacancy and so on have to be done using other sensitive techniques.

4 CONCLUSIONS

Mo(VI) in $\alpha\text{-MoO}_3$ can be substituted with Fe(III) up to an atomic fraction of $\text{Fe}/(\text{Mo}+\text{Fe})=0.1$ to form a solid solution and therefore to introduce the oxygen vacancy preferentially at the sites facing to van der Waals gap. Owing to the oxygen vacancy, the substitution of Mo(VI) with Fe(III) in $\alpha\text{-MoO}_3$ results in remarkable changes as a lithium insertion host, and the open-circuit potential becomes higher and the discharge capacity increases at the same time.

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