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# Lithium insertion into $(V_{1-y}Mo_y)_2O_5$

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## Abstract

The effects of structural modification caused by substitution of Mo for a part of V in  $V_2O_5$  on structural changes upon lithium insertion were investigated. For this purpose  $(V_{1-y}Mo_y)_2O_5$  ( $y = 0.25$ ) was synthesized, and its insertion behavior and structural changes upon lithium insertion were analyzed by XRD and ESR methods. In  $(V_{0.75}Mo_{0.25})_2O_5$ , the phases except for the starting material were not observed upon lithium insertion, and no phase transformation characteristics of  $V_2O_5$  occurred. From ESR measurement, a broad singlet signal of V(IV) was found, but those of Mo(V) were not detected. The line width of the signal V(IV) increased steeply at  $0.7 < x < 1$ . The open circuit potentials became less noble with increasing  $x$ , and dropped steeply at  $0.7 < x < 1$ . These dependencies closely correlate with structural changes estimated from results of ESR and XRD analyses. At  $2.7 < x$ ,  $\omega$ -phase oxide was formed. © 2001 Published by Elsevier Science B.V.

*Keywords:* Synthesized; Singlet; Analyzed

## 1. Introduction

$V_2O_5$  having a layered structure is of interest as an insertion cathode material for lithium secondary batteries. The structure of lithium inserted  $Li_xV_2O_5$  changes from  $\alpha$  through  $\varepsilon$  to  $\delta$  reversibly upon lithium insertion up to  $x = 1$ , where the structural change to  $\gamma$ -form occurs irreversibly. Further  $\gamma$ -form changes finally to  $\omega$ -form at  $x = 3$  [1].

The substitution of Mo for a part of V in  $V_2O_5$  causes changes in the structure, and at  $0 < y < 0.2$  in  $(V_{1-y}Mo_y)_2O_5$ , the oxide has a similar structure and discharge/charge characteristics as  $V_2O_5$ . Further substitution causes structural modifications, which have an effect on their discharge/charge behaviors [2]. Structural changes in these oxides upon lithium insertion were reported by the authors [3,4].

In this study, the effects of substitution of Mo for a part of V in  $V_2O_5$  on the structural changes upon lithium insertion were investigated further. For this purpose,  $(V_{0.75}Mo_{0.25})_2O_5$  was synthesized in powder form by the solid state reaction, and lithium insertion was carried out by chemical method. Electron spin resonance (ESR) and X-ray diffraction (XRD) measurements were used to analyze structural changes.

## 2. Experimental

### 2.1. Preparation of $(V_{0.75}Mo_{0.25})_2O_5$

A powder sample of  $(V_{0.75}Mo_{0.25})_2O_5$  was prepared by a solid state reaction of reagent grade  $V_2O_5$ ,  $V_2O_4$  and  $MoO_3$  powders. They were mixed at stoichiometric ratio in an agate mortar and the mixture was pressed (200 MPa) into pellets. The pellets were heated in evacuated ( $10^{-4}$  Torr) quartz ampoules at  $660^\circ\text{C}$  for 72 h [2] and then cooled down to room temperature at a rate of  $2^\circ\text{C}/\text{min}$ . The samples were identified by powder X-ray diffraction (XRD) measurement. XRD lines of the sample of  $(V_{0.75}Mo_{0.25})_2O_5$  were well described as monoclinic system by Rietveld analysis using the data reported by West et al. for  $y = 0.3$  [2], excepting weak peaks at  $40^\circ < 2\theta$ , which could presumably be ascribed to any one of  $V_9MoO_{40}$ ,  $V_{0.87}Mo_{0.13}O_{2.17}$  or  $V_2MoO_8$ .

The lattice parameters obtained in this work ( $a_0 = 11.74 \text{ \AA}$ ,  $b_0 = 3.639 \text{ \AA}$ ,  $c_0 = 4.210 \text{ \AA}$ ,  $\beta = 90.49^\circ$ ) coincide well with those obtained by West et al. [2].

### 2.2. Chemical lithiation

For chemical lithiation of  $(V_{0.75}Mo_{0.25})_2O_5$ ,  $n\text{-BuLi}/n\text{-hexane}$  was added to  $(V_{0.75}Mo_{0.25})_2O_5$  powder dispersed in  $n\text{-hexane}$  at various temperatures between 25 and  $85^\circ\text{C}$  under an argon atmosphere. The concentration of  $n\text{-BuLi}$

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was varied from 0.005 to 1.26 mol dm<sup>-3</sup> to control the extent of lithiation, which was determined by detecting lithium in the samples by the atomic absorption method, using an aqueous LiVO<sub>3</sub> solution as a standard. The extent of lithiation was designated by  $x = \text{Li}/2(0.75\text{V} + 0.25\text{Mo})$ .

### 2.3. The open circuit potential measurement

To prepare the electrode for the open circuit potential measurement in an inert atmosphere at 25°C, the electrode mixture of (V<sub>0.75</sub>Mo<sub>0.25</sub>)<sub>2</sub>O<sub>5</sub> and 10 wt.% polytetrafluoroethylene powders was pressed (200 MPa) into a pellet, the back face of which was connected to a lead wire with silver paste, and was covered with silicone rubber. A 1 mol dm<sup>-3</sup> LiClO<sub>4</sub> solution of propylene carbonate (PC) was used as the electrolyte. The reference and counter electrodes were metallic lithium wires.

### 2.4. Characterizations

Electron spin resonance (ESR) (JEOL JES-RE2X) and X-ray diffraction (XRD) (Rigaku-Denki RAD-C, CuKα, 40 kV, 20 mA) measurements were carried out at 25°C.

## 3. Results and discussion

The open circuit potentials of lithiated (V<sub>0.75</sub>Mo<sub>0.25</sub>)<sub>2</sub>O<sub>5</sub> were plotted against  $x$  in Fig. 1. In the composition region of about  $x < 1$ , the electrode potential became less noble with increasing  $x$ , as is typical of a solid state electrode. Between  $x = 0.7$  and 1.0, the electrode potential dropped rather steeply. Potential step at  $x = 1.0$  coincided with the composition at which all vanadium component became quadrivalent V(IV). Potential drop at V(IV)/V(V) = 1, typical

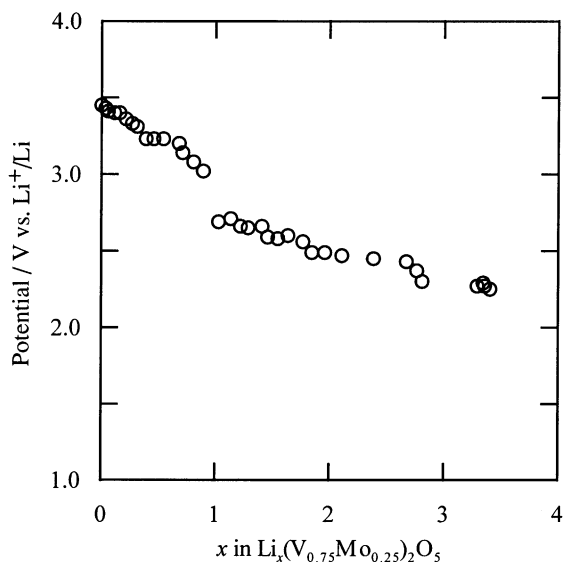


Fig. 1. Open circuit potentials for Li<sub>x</sub>(V<sub>0.75</sub>Mo<sub>0.25</sub>)<sub>2</sub>O<sub>5</sub>.

for other vanadium oxides [5] and also for (V<sub>0.9</sub>Mo<sub>0.1</sub>)<sub>2</sub>O<sub>5</sub> [4] was not observed. Further lithium insertion with decreasing potential with an easy slope at  $x > 1$  may cause reduction of V(IV) to V(III) and also presumably Mo(VI) to Mo(V).

As it is expected that V(V) is reduced to V(IV) and V(III), and Mo(VI) is reduced to Mo(V) with lithiation, the oxidation states of vanadium and molybdenum were investigated by ESR measurement. A broad singlet signal of V(IV) for lithiated oxides was found, but these of Mo(V) were not detected. Because signals of Mo(V) could be detected only with cryogenic temperature, only V(IV) was examined in this investigation. A change of line width of ESR spectra of V(IV) is shown in Fig. 2. Though  $g$  value of spectra did not change ( $g = 1.997$ ), line width became abruptly larger from about  $x = 0.7$ . Widening of the line width presumably was caused by a spin–spin interaction between neighboring V(IV) predominated at  $x = 0.7$ . Steep change in the open circuit potential at  $0.7 < x < 1$  may correlate to the widening of the line width at this composition. On further lithium insertion, a broad signal with a sharp signal ( $g = 2.046$ ) were observed in  $x = 2.67$ . The latter signal was ascribed to V(III). A similar phenomenon was observed in the case of  $\alpha$ -Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> at V(IV)/V(III) = 1 [6].

The structural changes of (V<sub>0.75</sub>Mo<sub>0.25</sub>)<sub>2</sub>O<sub>5</sub> upon lithiation were investigated by XRD measurement. At about  $x < 2.7$ , peaks except for the starting material were not observed, and no phase transformation characteristics of V<sub>2</sub>O<sub>5</sub> occurred. These results contrast to the case of (V<sub>0.9</sub>Mo<sub>0.1</sub>)<sub>2</sub>O<sub>5</sub> in which phase transformations typical for V<sub>2</sub>O<sub>5</sub> occur [4]. Then, at about  $2.7 < x$ , peaks ascribed to  $\omega$ -phase were observed. The changes in the lattice parameters were shown in Fig. 3. In the range of  $0.7 < x < 1.0$ , the lattice parameters,  $a$ ,  $c$  and  $\beta$  changed steeply compared to other composition regions. This phenomenon may correlate to the line widening and the O.C.P drop occurred at the same

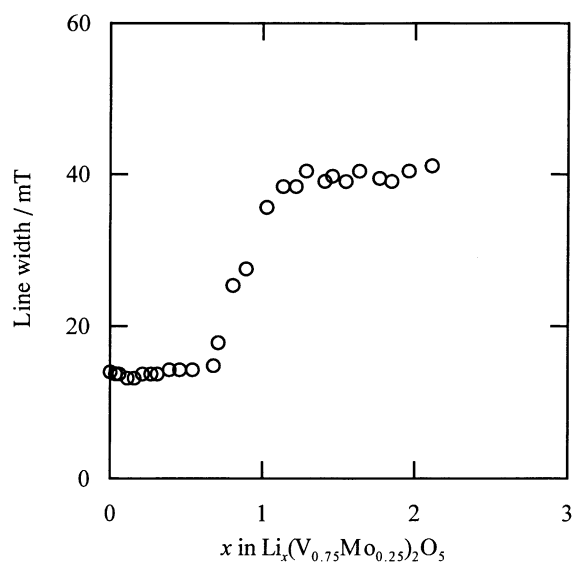


Fig. 2. Changes in the line width of V(IV) with  $x$  in Li<sub>x</sub>(V<sub>0.75</sub>Mo<sub>0.25</sub>)<sub>2</sub>O<sub>5</sub>.

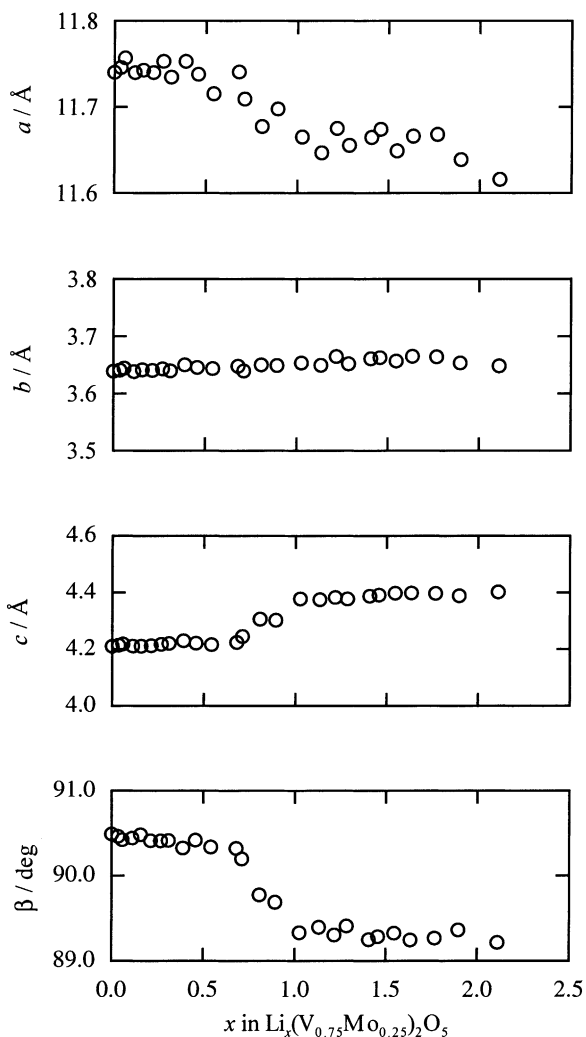


Fig. 3. Changes in the lattice parameters of  $a$ ,  $b$ ,  $c$  and  $\beta$  with  $x$  in  $\text{Li}_x(\text{V}_{0.75}\text{Mo}_{0.25})_2\text{O}_5$ .

composition region. The change in crystal structure of the starting oxide characterized mainly by increase in  $c$  axis, i.e. expansion of the interlayer. The crystal structure itself was not transformed, up to  $2.7 < x$ , where  $\omega$ -phase oxide with the rock salt structure was formed from directly original monoclinic structure without any previous phase transformation.

#### 4. Conclusion

By a chemical lithiation to complex oxide  $(\text{V}_{0.75}\text{Mo}_{0.25})_2\text{O}_5$  which substituted molybdenum for one part of vanadium of  $\text{V}_2\text{O}_5$ , it was revealed that  $(\text{V}_{0.75}\text{Mo}_{0.25})_2\text{O}_5$  did not behave like as  $\text{V}_2\text{O}_5$ , and the interlayer expanded at  $0.7 < x < 1$ . Further insertion caused a formation of  $\omega$ -phase oxide with rock salt structure at  $2.7 < x$ . Phase transformation typical for  $\text{V}_2\text{O}_5$  upon lithium insertion occurred only for the oxides with  $\text{V}_2\text{O}_5$ -like  $\text{VO}_5$  arrangement in the layer.

#### References

- [1] C. Delmas, H. Cognac-Auradou, J.M. Cocciantelli, M. Ménérier, J.P. Doumerc, *Solid State Ionics* 69 (1994) 257.
- [2] K. West, B. Zachau-Christiansen, S. Skaarup, T. Jacobsen, *Solid State Ionics* 53 (1992) 356.
- [3] M. Eguchi, F. Maki, H. Kimura, K. Takahashi, in: *Proceedings of Symposium of Annual Fall Meeting of ECS on Intercalation Compounds for Battery Materials*, Honolulu, Hawaii, 1999, p. 230.
- [4] M. Eguchi, F. Maki, H. Kimura, H. Takahashi, Y. Momose, *Electrochemistry* 68 (6) (2000), in press.
- [5] B. Pecquenard, D. Gourier, N. Baffler, *Solid State Ionics* 78 (1995) 287.
- [6] M. Eguchi, T. Miura, T. Kishi, *Denki Kagaku* 62 (1994) 504.