

INSERTION OF LITHIUM INTO VANADIUM MOLYBDENUM OXIDES

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Summary

Chemical insertion of lithium into V_2O_5 , $Mo_{0.1}V_{1.8}O_{4.8}$ and MoV_2O_8 by LiI has been investigated. The limiting lithium content in all oxides is $Li/V = 0.5$, suggesting that only the V component is responsible for the lithium insertion. For V_2O_5 , two potential plateaux correspond exactly to two-phase coexistent crystal structures with different van der Waals gap distances; the interaction energy between inserted lithium is attractive. By contrast, as the ratio of V substitution in Mo increases, the two-phase behaviour decreases, and the interaction between Li^+ cations becomes repulsive. These insertion characteristics have been analyzed in relation to structural changes in VO_5 polyhedra.

Introduction

Vanadium pentoxide, V_2O_5 , is a material of interest for application in secondary lithium battery systems [1, 2], because of its noble potential against Li^+/Li and its specific feature of having a potential that is independent of the lithium content.

In this work, experiments have been conducted to obtain a more precise correlation between the electrode potential and the lattice parameters of $Li_xV_2O_5$ and to determine the role of structural changes in VO_5 polyhedra that arise from the coordination of inserted Li^+ . The former objective has involved studies of the chemical insertion of lithium into V_2O_5 and other oxides through the reaction of LiI with the oxides in acetonitrile. For the second objective, the V atoms in V_2O_5 have been substituted by Mo atoms in order to cause a change in the $V=O$ bond strength. The oxides used were $Mo_{0.1}V_{1.8}O_{4.8}$ (same structure as V_2O_5 , the size of the block of corner sharing octahedra is $2 \times \infty \times \infty$) and MoV_2O_8 ($3 \times \infty \times \infty$) [3].

Experimental

The chemicals used in sample preparation were: reagent grade V_2O_5 (Soekawa Chemicals), molybdenum trioxide, MoO_3 (Kanto Chemical), and

LiI (Yanagishima Pharmaceutical). The synthesis of MoV_2O_8 and $\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$ involved mixing appropriate amounts of V_2O_5 and MoO_3 and then heating up to 650°C (700°C in the case of $\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$) at a rate of $10^\circ\text{C min}^{-1}$ in air. After maintaining this temperature for 3 h, the mixture was cooled to 400°C (450°C for $\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$) for 4 h.

The lithium bronze ($\text{Li}_x\text{V}_2\text{O}_5$) was prepared using the technique described by Murphy *et al.* [4], *i.e.*, oxide (1.5 mmol) was added to an acetonitrile solution (25 ml) of LiI. After 3 days' reaction, the product was separated by filtration and washed with acetonitrile. The x -values of the Li bronzes were determined by titrating the product I_2 with a standard aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. $\text{Li}_x\text{V}_2\text{O}_5$ was also prepared by the addition of a 15% hexane solution of $n\text{-BuLi}$ (Tokyo Kasei Kogyo) to V_2O_5 .

Potential measurements were carried out with pelletized Li bronzes using the cell: $\text{Li}_{0.54}\text{V}_2\text{O}_5/1\text{ M LiClO}_4$ in PC/ Li_xMeO_y . The potential values are reported here with reference to $1\text{ M Li}^+/\text{Li}$.

Results and discussion

The chemical insertion of lithium into V_2O_5 , $\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$, and MoV_2O_8 using LiI solution can be expressed by:



The upper limit of insertion into these oxides was found to be $\text{Li}/\text{V} = 0.5$ in all cases. It can therefore be concluded that the V atom is responsible for the reduction through lithium insertion.

The open-circuit potential (U) of $\text{Li}_x\text{V}_2\text{O}_5$ as a function of Li/V is shown in Fig. 1. The values of U coincide with those reported by Dickens *et al.* [5], and two-phase behaviour is clearly observed in the regions of $0.05 \leq \text{Li}/\text{V} \leq 0.25$ and $0.25 \leq \text{Li}/\text{V} \leq 0.5$. In these regions, the lattice

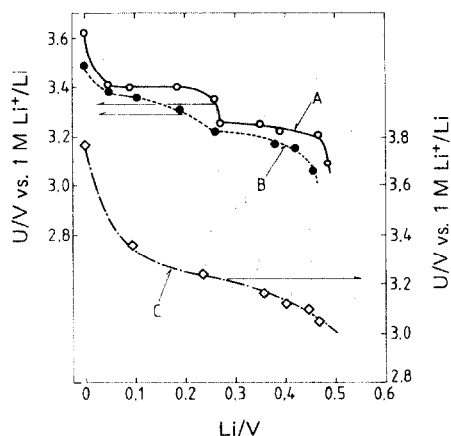


Fig. 1. Dependence of U on Li/V . (A), $\text{Li}_x\text{V}_2\text{O}_5$; (B), $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$; (C), $\text{Li}_x\text{MoV}_2\text{O}_8$.

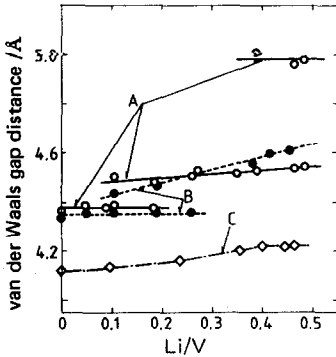


Fig. 2. Dependence of van der Waals gap distance on Li/V. (A), $\text{Li}_x\text{V}_2\text{O}_5$; (B), $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$; (C), $\text{Li}_x\text{MoV}_2\text{O}_8$.

constant b_0 , which corresponds to a van der Waals gap into which lithium ions are inserted, has split values (Fig. 2). Each split value of b_0 corresponds to a respective potential plateau, and demonstrates the co-existence of two layered structures with different van der Waals gaps. This dependence of b_0 on x differs from the findings of Murphy *et al.* [4] and Takasu *et al.* [2] in that these authors did not report the third phase having a b_0 value of 0.497 \AA in the $\text{Li}/\text{V} < 0.5$ region.

The thermodynamic equation for the electrode potential is [6]:

$$U = U_0 + Ky - (RT/F) \ln[y/(y_{\max} - y)] \quad (2)$$

where y and $(y_{\max} - y)$ are the fractions of occupied and the unoccupied sites, respectively, and K is the energy term arising from interactions between guest species. Estimating y_{\max} to be 0.265 from the data in Fig. 1, $U + (RT/F) \ln[(\text{Li}/\text{V})/(0.265 - \text{Li}/\text{V})]$ is found to be linear with Li/V (as shown in Fig. 3) and the slope of this relationship yields a value of K of $+0.38 \text{ eV}$. The positive value of K indicates that the interaction between lithium cations is attractive, and comparing these data with those of the b_0 -stage

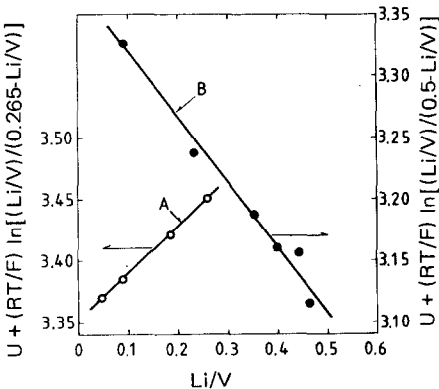


Fig. 3. Dependence of $U + (RT/F) \ln[y/(y_{\max} - y)]$ on $y (= \text{Li}/\text{V})$. (A), $\text{Li}_x\text{V}_2\text{O}_5$ ($y_{\max}; \text{Li}/\text{V} = 0.265$); (B), $\text{Li}_x\text{MoV}_2\text{O}_8$ ($y_{\max}; \text{Li}/\text{V} = 0.5$).

phenomenon which takes place in $\text{Li}_x\text{V}_2\text{O}_5$ shows that Li^+ cations are coordinated at all trigonal prism sites [7] in van der Waals gaps on alternate layers for $\text{Li}/\text{V} \approx 0.25$, and on every layer for $\text{Li}/\text{V} \approx 0.5$.

The potential-composition curve for $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$ is shown in Fig. 1 (curve B). By comparison with the curve for $\text{Li}_x\text{V}_2\text{O}_5$ (curve A), it appears that substitution of part of the V with Mo results in a decline in the two-phase behaviour. In the case of $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$, a b_o value corresponding to the third phase is not observed and the increase in b_o in the second phase is steeper, so that the system behaves like a solid-solution electrode (Fig. 2). The dependence of potential on composition is therefore expressed by [6]:

$$U = U_o - (RT/F) \ln[y/(y_{\max} - y)] \quad (3)$$

This relationship is shown in Fig. 4, again taking y_{\max} as 0.267 from the data in Fig. 1. The linear relationship has a slope of nearly RT/F . This indicates that the interaction between inserted guests is minimal ($K \sim 0$), and therefore stage phenomena caused by the attractive interaction between the guests does not occur.

The values of U_o in eqns. (2) and (3) are 3.35 V for $\text{Li}_x\text{V}_2\text{O}_5$ and 3.34 V for $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$. These values indicate that the host-guest interaction does not change on introducing Mo atoms into the host. Moreover, as the lattice spacings are virtually unaltered on introducing Mo atoms in the $\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$ range, the change in interaction energy between the guests is probably due, in part, to an inhomogeneity of the host lattice that is caused by introducing Mo atoms and which forces the inserted Li^+ ions into a random distribution.

The potential-composition curve for $\text{Li}_x\text{MoV}_2\text{O}_8$ (curve C, Fig. 1) is characteristic of solid-solution electrodes; two-phase behaviour is not observed. The lattice constant c_o , corresponding to a van der Waals gap, increases with insertion of lithium in the region $0 < \text{Li}/\text{V} < 0.4$, as shown in Fig. 2. The relation between potential and composition in the case of $\text{Li}_x\text{MoV}_2\text{O}_8$ (Fig. 3) is expressed by eqn. (2), if y_{\max} is taken as 0.5 from the data in Fig. 1. The value of K is found to be -0.52 eV. The negative sign of K suggests that the interaction between Li^+ cations is repulsive, and therefore random distribution of inserted guests occurs, as expected from

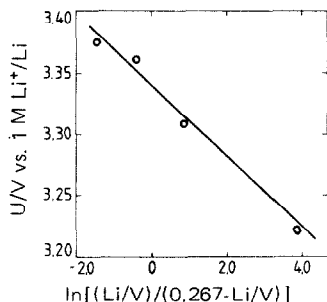


Fig. 4. Dependence of U on $\ln[(\text{Li}/\text{V})/(0.267 - \text{Li}/\text{V})]$ in $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$.

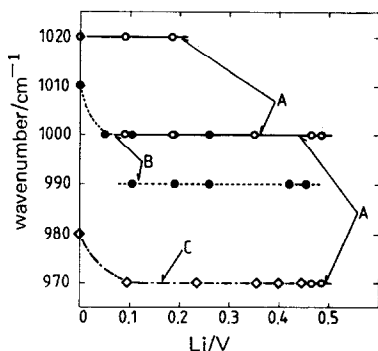


Fig. 5. Dependence of wavenumber corresponding to V=O stretching mode on Li/V. (a), $\text{Li}_x\text{V}_2\text{O}_5$; (B), $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$; (C), $\text{Li}_x\text{MoV}_2\text{O}_8$.

the continuous increase in the lattice parameter c_0 (Fig. 2). The value of U_0 calculated from eqn. (2) for MoV_2O_8 is 3.37 V, which indicates that the host-guest interaction is almost the same as that in $\text{Li}_x\text{V}_2\text{O}_5$.

The dependence on Li/V of the wavenumber corresponding to the V=O stretching vibration mode is given in Fig. 5. With V_2O_5 , the absorption band located at 1020 cm^{-1} for the V=O stretching vibration mode [8] is shifted to 980 cm^{-1} by molybdenum substitution. Lithium insertion causes a decrease in the wavenumber, notably in a stepwise manner with $\text{Li}_x\text{V}_2\text{O}_5$ and $\text{Li}_x\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$. As the MoV_2O_8 crystal has a longer, and therefore weaker, V=O bond (bond distance: 1.644 or 1.701 Å [9]), donation of electrons from the inserted lithium to the vanadium will affect the V=O bonding state less than in the case of $\text{Li}_x\text{V}_2\text{O}_5$. Therefore, new phase formations or analogous phenomena, as indicated by an interaction term between the guests, do not occur. By contrast, the stronger V=O bond of $\text{Li}_x\text{V}_2\text{O}_5$ (bond distance: 1.585 Å [10]) is much more influenced by donation of electrons from the inserted lithium to the vanadium, and this will cause stepwise changes in the V=O bonding state accompanied by regular rearrangement of lithium ions to cause the stage effect. This phenomenon will be minimized by substitution of Mo in the $\text{Mo}_{0.1}\text{V}_{1.8}\text{O}_{4.8}$ range, as is seen in Fig. 5. Changes in the V=O bond distance by the acceptance of electrons can be explained as follows. In V_2O_5 , the V^{5+} ion is surrounded by five oxygen atoms [9]. When electrons are donated to the empty d orbital by the insertion process, the VO_5 square pyramid stretches along its b axis (*i.e.*, Jahn-Teller effect). This results in an increase in the V=O distance, and induces abrupt increases in the van der Waals gap and stage phenomenon. Molybdenum substitution minimizes this effect.

From the above findings, it is concluded that the insertion process of lithium and the accompanying phenomena are controlled not by elastic interaction between the host and guest species, but by structural changes in the host through the acceptance of electrons by vanadium from the inserted lithium.

Conclusion

With lithium insertion into vanadium molybdenum oxides, the host-guest interaction does not change on introducing Mo atoms into the host, while structural changes in the host polyhedra through the acceptance of electrons by the insertion process are minimized and an abrupt increase in the van der Waals gap is not observed.

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