Lithium Insertion Characteristics of α - $\text{Cu}_2\text{V}_2\text{O}_7$

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Lithium insertion characteristics of a complex oxide containing V(V), α - $\text{Cu}_2\text{V}_2\text{O}_7$, were investigated. Lithium insertion was carried out chemically using an *n*-BuLi/hexane solution and also by the electrochemical GITT method comparatively. The valence states of copper or vanadium and the structural changes by lithium insertion were analyzed by ESR and XRD measurements, respectively. It was revealed that reduction processes occurred stepwisely with an increasing extent of lithium insertion, x in α - $\text{Li}_x\text{Cu}_2\text{V}_2\text{O}_7$. Up to $x=1$, a half of Cu(II) was reduced preferentially to Cu(I). Remaining Cu(II) and a half of V(V) were reduced at $1 < x < 3$, and equimolar V(V) and V(IV) coexisted in addition to Cu(I) at $x=3$. At $x > 3$, further, the reduction both of V(V) beyond V(IV)/V(V)=1 and of Cu(I) to Cu(0) occurred.

1 INTRODUCTION

Vanadium pentoxide (V_2O_5) crystal has relatively strong interlayer interaction owing to the partial ionicity of intralayer covalent bonds, and its van der Waals gap can accept only small ions such as protons (H^+) and lithium ions (Li^+) in the intercalation reactions at an ambient temperature. Moreover, this strong interlayer interaction causes a discontinuous change in interlayer distance even at a small level of lithium insertion. This contrasts to a case of VOPO_4 with the weaker interlayer interaction, where insertion of even larger guests occurs easily^{1, 2)}. More drastic conditions are required to insert sodium ions to V_2O_5 , and introduction of ionic character in the interlayer causes a change in the characteristics for succeeding lithium insertion³⁾.

More complex cases were reported, where V_2O_5 layers were bound together with foreign metal ions through the bonds sharing oxygen with vanadium ions with a covalent character more or less. As a typical example of such systems, Yamaki *et al.* investigated the discharge-charge characteristics of $n\text{CuO}-\text{V}_2\text{O}_5$ ($n=1, 2$ and 5) as a positive pole material for a lithium battery⁴⁻⁸⁾. They showed that lithium insertion occurred comparatively easily leading to a small expansion of the interlayer spacing, and that Cu(II) in the oxide participated in the redox reactions to form metallic copper. Messina *et al.*, on the other hand, examined the electrochemical behaviors of the multi-phase $\text{CuO}+\text{V}_2\text{O}_5$ system of various $\text{CuO}/\text{V}_2\text{O}_5$ ratios⁹⁾ and pointed out that Cu(II) took part in the reduction of the host upon lithium insertion. This phenomenon may be interesting also from a practical view point to increase redox capacity of positive pole material for a lithium battery. Similar redox reac-

tions were reported, further, also for the $\text{Ag}_2\text{O}-\text{V}_2\text{O}_5$ system^{10, 11)}.

In this investigation, an attempt was made to analyze the behavior of redox system incorporated in the layered structure of vanadium (V) oxides in conjunction with redox reactions of V(V) in the host lattices. For this purpose, changes in valence states and in the crystal structure of α - $\text{Cu}_2\text{V}_2\text{O}_7$ after lithium insertion were examined.

2 EXPERIMENTAL

Host material, α - $\text{Cu}_2\text{V}_2\text{O}_7$, was prepared by a solid state reaction of reagent grade CuO and V_2O_5 powders as described by Yamaki *et al.*⁴⁾. Powdered CuO was mixed with V_2O_5 at a molar ratio of 2:1 in an agate mortar and the mixture was pressed (200 MPa) into pellets. They were heated at 620°C on a platinum plate for 24 h in air and then cooled down to room temperature at a rate of 2°C/min. The samples obtained were analyzed by powder X-ray diffraction (XRD) measurements and confirmed to be a single phase of α - $\text{Cu}_2\text{V}_2\text{O}_7$ referring to JCPDS data (No.26-566).

For chemical insertion of lithium into α - $\text{Cu}_2\text{V}_2\text{O}_7$, *n*-BuLi/*n*-hexane was added as a reducing agent for α - $\text{Cu}_2\text{V}_2\text{O}_7$ powder dispersed in *n*-hexane at 25°C under N_2 atmosphere. The concentration of *n*-BuLi was varied from 0.03 to 1.60 mol·dm⁻³ to control the extent of lithium insertion. Hereafter, the extent of lithium insertion was indicated by x in α - $\text{Li}_x\text{Cu}_2\text{V}_2\text{O}_7$, which was obtained by determining lithium in the samples by the atomic absorption analysis using an aqueous LiVO_3 solution as a standard.

To prepare the electrode for the potential measurement in an inert atmosphere at 25°C, α - $\text{Li}_x\text{Cu}_2\text{V}_2\text{O}_7$ was powdered and then pressed (200 MPa) into a pellet, the back face of which was connected to a lead wire with silver paste. A 1 mol·dm⁻³ LiClO_4 solution of propylene carbonate (PC) was used as the electrolyte. The reference electrode was a metallic lithium wire.

Both XRD and electron spin resonance (ESR) measurements were carried out at 25°C.

Further, electrochemical insertion of lithium to

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Fig. 1 ESR spectra of $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$
 1: $x=0$, 2: $x=0.48$, 3: $x=0.99$, 4: $x=1.40$,
 5: $x=2.50$, 6: $x=3.18$, 7: $x=4.26$.

Fig. 2. Change in the g -value of Cu(II) with x in $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

$\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ was carried out as a comparison. In this case, powdered $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (or $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$) was mixed with 30 wt% swelling graphite (Nippon Carbon Co., Ltd.), and a pellet electrode was prepared by the same way as described above. A $1 \text{ mol}\cdot\text{dm}^{-3} \text{LiClO}_4/\text{PC}$ solution was used as the electrolyte. The reference and the counter electrodes were metallic lithium wires. All procedures were carried out under an inert atmosphere. The galvanostatic intermittent titration technique (GITT) was employed for lithium insertion at a current density of $-0.4 \text{ mA}\cdot\text{cm}^{-2}$.

Fig. 3 Dependence of integrated intensity of ESR signal of Cu(II) on x in $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

3 RESULTS AND DISCUSSION

3.1 ESR spectra of chemically prepare $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

The rate of chemical lithium insertion to $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ seems to slow down at $1 < x$. For lithium insertion to $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, the valence states of both V(V) and Cu(II) become lower, and hence the ESR measurement can be expected as a useful tool to detect these changes as both V(IV) and Cu(II) are ESR-active. Some typical ESR spectra of $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ and lithiated samples are shown in Fig. 1. The spectrum of $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ with a broad signal is considered to arise from Cu(II) after the observation by Sunandana *et al.*¹²⁾. With increasing x , the shapes of spectra remain almost unchanged up to about $x=1$ accompanying slight hyperfine signal with increasing x as mentioned below, whereas the main signal intensities decrease gradually. The g -values of these main signals are about 2.14 and almost independent of x in this range as seen in Fig. 2. The latter fact suggests that the coordination of Cu(II) in the crystal lattice remains unchanged with increasing x .

To estimate the concentration of remaining Cu(II), the integrated intensities of these main signals are shown in Fig. 3, where the intensity decreases monotonously with x up to $x=1$. This means that the reduction of Cu(II) to Cu(I) occurs preferentially in the first stage of lithium insertion up to $x=1$, where a half amount of Cu(II) changes to Cu(I). The broad single line for Cu(II) is attributed to the existence of interacting Cu(II) species in the lattice, and the isolation of Cu(II) species through reduction would cause a much

Fig. 4 Assignment of hyperfine signals in the spectrum of α - $\text{Li}_{1.18}\text{Cu}_2\text{V}_2\text{O}_7$

Fig. 5 Change in the g -value of V(IV) with x in α - $\text{Li}_x\text{Cu}_2\text{V}_2\text{O}_7$ ($\circ$: $g_{//}$, $\square$: $g_{\perp}$)

decrease in the intensity than expected from the concentration of Cu(II).

The shapes of ESR spectra change rather discontinuously at about $x=1$ and then become more complicated with increasing x at $1 < x$. These spectra are considered as an overlap of two kinds of V(IV) signals. As shown in Fig. 4, a signal of hyperfine structure of eight components characteristic for V(IV) is observed in the spectra at $x > 1$. The average $g_{//}$ - and $g_{\perp}$ -values determined at $1 < x < 4$ are 1.923 and 1.964, respectively, as seen in Fig. 5. Both the signal shape and the hyperfine structure constants (average values; $A_{//}=18.01$, $A_{\perp}=6.187$, independent of x) are in agreement with the data reported for V(IV) in VO^{2+} by Ueda *et*

Fig. 6 Dependence of integrated intensity of ESR signal of V(IV) on x in α - $\text{Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

*al.*¹³. This fact suggests that the partially dissociated VO^{2+} unit forms in the oxide by the reduction of V(V) to V(IV). The g -value of a broad singlet signal is 1.976, on the other hand, which may be attributed to V(IV) formed in the VO_4 lattice units after Takahashi *et al.*¹⁴. Thus, the spectra at $x > 1$ indicate the existence of two kinds of V(IV), i.e., V(IV) in the lattice and V(IV) in the dissociated form of VO^{2+} . The hyperfine ESR signals were found out together with a broad signal by Gourier *et al.*¹⁵ in case of lithium insertion to V_2O_5 . Whittington *et al.*¹⁶, further more, obtained similar spectra in some vanadium catalysts supported on silica and other carriers, and they attributed the hyperfine spectra having different $g_{//}$ - and $g_{\perp}$ -values to the presence of "isolated vanadyls (V(IV)=O) with restricted motion" and the broad single line of "interacting V(IV)".

At $1 < x < 3$, the integrated intensity of the V(IV) signal increases with x as seen in Fig. 6, showing that the reduction of V(V) to V(IV) occurs preferentially. At about $x > 2$, further, the increment of the intensity of V(IV) tends to decrease, and this suggests that the reduction of Cu(II) to Cu(I) occurs competitively.

At the same time, the hyperfine structure of V(IV) can be observed slightly at $x < 1$ as mentioned above. These facts show that the reduction processes of Cu(II) and V(V) overlap each other slightly in the composition range $0 < x < 2$.

3.2 XRD patterns of chemically prepared α - $\text{Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

In the reduction processes of copper and vanadium components on lithium insertion, the struc-

Fig. 7 XRD patterns of $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

1: $x=0$, 2: $x=0.99$, 3: $x=1.40$,
4: $x=2.50$, 5: $x=3.05$, 6: $x=4.26$

Fig. 8 Changes in the spacings of (420) and (202) faces ($\circ$: $g_{||}$, $\square$: $g_{\perp}$)

tural changes of $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ are investigated by XRD measurements, and typical XRD patterns are given in Fig. 7. With increasing value of x , XRD lines, though remaining at the original positions, become broader gradually and the crystal lattice

Fig. 9 Dependence of the open circuit potential on x in $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

$\circ$: chemical, $\square$: electrochemical insertion

tends to be disordered. The lattice spacing calculated from the strongest (420) and (202) diffraction lines are unchanged at $x < 1$ as shown in Fig. 8, where the latter corresponds to the interlayer spacing. Therefore, a change in the interlayer distance is not remarkable at $x < 1$. In this composition range, preferential changes of the planes including CuO_6 units, which are expected to release Jahn-Teller distortion by the reduction of Cu(II) to Cu(I) , are not observed. Yamaki *et al.* reported that shifts of the (420) peak from $2\theta = 27.3^\circ$ to 26.8° and of the (202) peak from 29.0° to 28.9° after discharge of 2.0 Li equivalent⁴). These shifts correspond, however, only to small changes in the lattice spacings, i.e., ca. $0.01 \text{ \AA}$ for (420) spacing, and these data are not inconsistent with those cited in Fig. 8. The most remarkable change in XRD lines after lithium insertion is observed at around $2\theta = 43^\circ$ ((622) peak). A new broad peak at around $2\theta = 42.3^\circ$ appears at about $x = 1$ and becomes intense gradually with increasing x and at the same time the peak at 44.0° becomes weaker. The intensity of the original line at $2\theta = 36.2^\circ$ (corresponding to (222) face) remains unchanged, whereas those of other lines lower. These changes in the diffraction lines will be a result of a topotactic change in the lattice containing some preferential faces, maintaining the original mother lattice structure. Details of the change in the lattice structure remain unclear and further analyses are necessary. At $x > 3$, finally, broad diffraction lines observed at $2\theta = 43^\circ$, 50° and 74° (indicated by arrow heads in Fig. 7) correspond to (111), (200) and (220) faces of metallic copper, respec-

Fig. 10 Relation between $E + (RT/F) \ln(x'/1-x')$ and x ($x' = x/x_{\max}$ with $x_{\max} = 1.0$)

tively, suggesting the reduction of Cu(II) to Cu(0) to occur.

3.3 The open-circuit potential of $\alpha\text{-Li}_x\text{Cu}_2\text{V}_2\text{O}_7$

The open-circuit potentials of lithium insertion compounds in a $1 \text{ mol} \cdot \text{dm}^{-3} \text{LiClO}_4/\text{PC}$ solution are plotted against x in Fig. 9. In a range of $0 < x < 1$, the electrode potential is expected to obey the Nernst's equation as recognized from Fig. 10. Accordingly, lithium ions behave like as an ideal solute with negligible inter-guest interaction in this single phase region of $0 < x < 1$.

The electrode potential vs. x curve at $1 < x < 3$ becomes flat more or less, where a topotactic change presumably occurs. Furthermore, the electrode potential drops steeply at $x \approx 3$. This seems to be a similar phenomenon to that observed for V_2O_5 and other various V(V) oxides at the reduction stage of $\text{V(IV)}/\text{V(V)} = 1^{17)}$. Hence, a half of V(V) probably remains in the oxide at $x = 3$ in the present case.

The electrode potentials of electrochemically lithium inserted samples are compared also in Fig. 9. These data are in fair agreement with those of chemically inserted samples, and it is confirmed that the same intercalation compounds are prepared by both methods.

4 CONCLUSIONS

The reduction of V(V) and Cu(II) in the host lattice occurs successively as confirmed clearly by ESR spectra, though the overlapping of each reduction step occurs to some extent: (1) a half of Cu(II) is reduced to Cu(I) at $x = 1$, (2) remaining Cu(II) and the first half of V(V) are reduced to Cu(I) and V(IV), respectively, up to $x = 3$, where only a small amount of Cu(0) is formed, (3) the V(IV)/V(V) ratio decreases from unity gradually with increasing x beyond three.

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