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Preparation and Electrochemical Properties of Li-V Oxides by the Reaction of an Aqueous Hydrogen Peroxide Solution with Metal Alkoxides

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Lithium vanadium (Li-V) oxides have been prepared by the direct reaction of an aqueous hydrogen peroxide solution with lithium and vanadium alkoxides, $LiO\text{-}n\text{-}C_3H_7$ and $VO(O\text{-}i\text{-}C_3H_7)_3$. It is confirmed that three distinct crystal phases (α, β and γ) having the general formula of $Li_xV_2O_5$ ($0 \le x < 3$) can be prepared by increasing the amount of added $LiO\text{-}n\text{-}C_3H_7$. Besides these phases, the production of $LiVO_3$ and Li_3VO_4 is also confirmed. The varieties of the products are very similar to those of the products prepared by the solid state reaction of Li_2CO_3 with V_2O_5, etc., at ~600 °C. Lithium charge measurements of the γ phase with the formula of $Li_{2.2}V_2O_5 \cdot 0.9H_2O$ have been carried out to investigate its electrochemical properties.

Key word: Li-V oxides, Hydrogen peroxide, Metal alkoxides, Lithium intercalation properties

1. INTRODUCTION

Lithium vanadium (Li-V) oxides are of interest as a promising candidate for the positive electrode material of lithium secondary batteries and electrochromic display devices [1-3]. There have been numerous studies pertaining to the electrochemical lithium intercalation behavior in the Li-V oxides. In practice, however, secondary cells using the Li-V oxides have been still prohibitive for wide commercial applications because of their poor cycle life, etc.

While several phases have been reported for the Li-V oxides having the general formula of $Li_xV_2O_5$, it is commonly accepted that the α ($0 \le x \le 0.1$), ε ($0.35 \le x \le 0.7$), δ ($0.9 \le x \le 1$), γ ($1 \le x \le 2$), ξ ($2 \le x \le 3$), and ω (x = ~3) phases appear with an increase in the lithium content x during the electrochemical lithium intercalation process [4,5]. These phases, except for the ω phase, primarily have two-dimensional layer structures [6], whereas the ω phase is considered to have a cubic rocksalt-type structure [7]. It is widely known that the ω phase has excellent charge and discharge properties; it is very stable even at a low voltage without structure modifications and has a good cycle property [7]. Thus, the ω phase is considered as the key material for wide commercial applications of the Li-V oxides.

However, at present, the ω phase can only be obtained by limited techniques such as electrochemical and chemical lithium intercalations [8]. Moreover, these techniques are unsuitable for large-scale preparation with no impurities. From this point of view, we have initiated a study to directly prepare the ω phase by a kind of sol-gel process. The characteristic of this preparation is the direct reaction of an aqueous hydrogen peroxide (H_2O_2) solution with the lithium and vanadium alkoxides. Recently, we have successfully prepared several kinds of Li-V oxides using this preparation method.

In this study, we first demonstrate the preparation of the Li-V oxides and then the electrochemical properties of the obtained γ phase.

2. EXPERIMENTAL

The Li-V oxides were prepared by the reaction of an aqueous H_2O_2 solution with the lithium and vanadium alkoxides, $LiO\text{-}n\text{-}C_3H_7$ and $VO(O\text{-}i\text{-}C_3H_7)_3$ [9,10]. Figure 1 illustrates the diagram for the preparation of the Li-V oxides. $LiO\text{-}n\text{-}C_3H_7$ and $VO(O\text{-}i\text{-}C_3H_7)_3$ were proportionally weighted for values of x = 0 – 4 with intervals 0.5 for the general formula of $Li_xV_2O_5$. Each weight quantity of the alkoxides was dissolved in a small amount of 2-ethoxyethanol ($C_2H_5OCH_2CH_2OH$). The mixtures were added in limited amounts to an aqueous 30% H_2O_2 solution, then refluxed at ~100 ° C for 3 h. Subsequently, the excess H_2O_2 in the mixtures was decomposed with several platinum foils, and the organic residue was removed by extraction with diethyl ether. Finally, the mixtures were filtered off and dried at 120 °C to produce the Li-V oxide powders.

X-ray diffraction (XRD) and thermogravimetry (TG) measurements were carried out to evaluate the phases and the water contents of the products, respectively. In addition, the lithium contents of the products were determined using an atomic adsorption spectrometry method.

The lithium charge measurements were carried out to investigate the electrochemical properties of the Li-V oxides. For the measurements, the γ phase with the general formula of $Li_{2.2}V_2O_5 \cdot 0.9H_2O$, prepared by heat-treatment at 300 °C under an argon atmosphere, was used as the material for the working electrode. The working electrode was prepared as follows. A mixture of the γ phase powder, acetylene black and poly(vinylidene fluoride) having a weight ratio of 8 : 1 : 1, formed by kneading with a small amount of n-methyl pyrrolidone, was spread on an aluminum foil and heated at 150 °C for 30 min under vacuum. A solution of 1M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) having a volume ratio 3 : 7 was used as

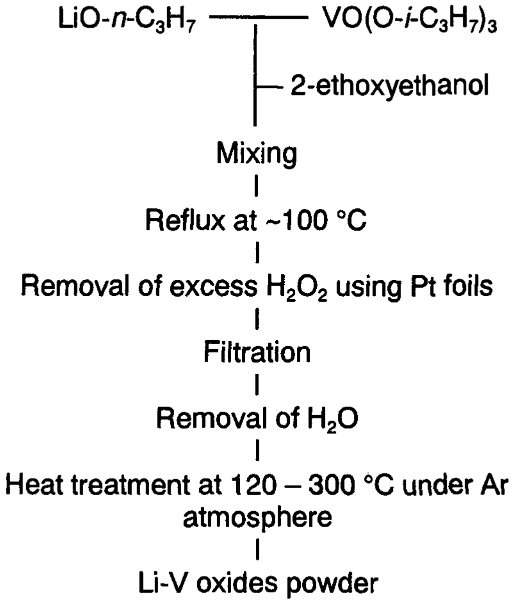

Figure 1. Flow diagram for the preparation of Li-V oxides.

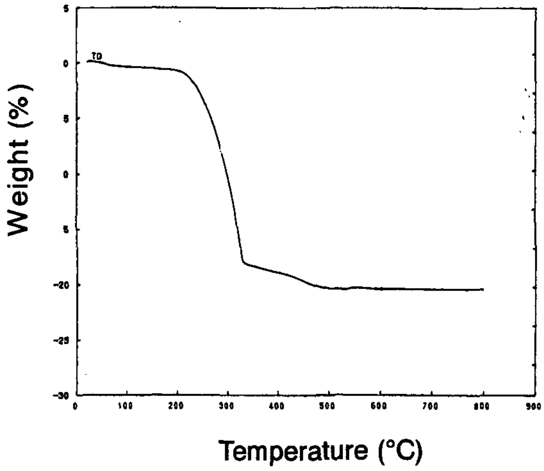

Figure 2. A typical TG curve for the as-prepared Li-V oxide having the general formula of $Li_3V_2O_5{\cdot}nH_2O$ obtained by the heat-treatment at 120 °C.

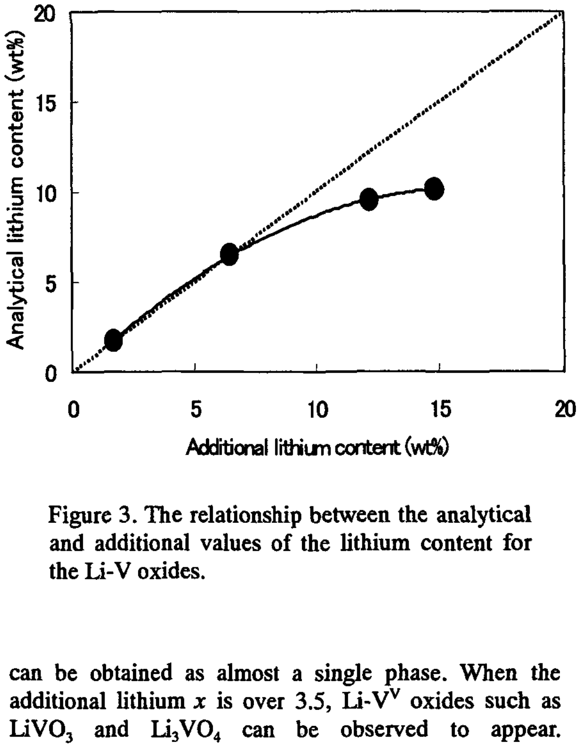

Figure 3. The relationship between the analytical and additional values of the lithium content for the Li-V oxides.

the electrolyte of the cell. The measurements were carried out at a constant current density of ±50 μA·dm^{-2} using a two-electrode cell equipped with a lithium foil as the counter electrode.

3. RESULTS AND DISCUSSION

In general, many metal oxides prepared by the sol-gel process and heat-treatment at low temperature below ~400 °C have water of crystallization and/or adsorbed water [11]. A similar situation is possible for the as-prepared materials in this study. Figure 2 shows a typical TG curve for the as-prepared Li-V oxide having the general formula of $Li_3V_2O_5{\cdot}nH_2O$ obtained by heat-treatment at 120 °C. As shown in Fig. 2, there is an almost one-step weight loss of ~20% during the heating process between about 200 – 320 °C, which is considered to correspond to the release of water. It is also confirmed that such weight losses are observed for all the other specimens. From the TG curves, the water content n in $Li_xV_2O_5{\cdot}nH_2O$ ($0 \leq x \leq 4$) was found to be 2.4.

The relationship between the analytical and additional values of the lithium content for the Li-V oxides is given in Fig. 3. As shown in Fig. 3, the analytical values are almost identical with the additional ones up to ~7wt%, and then tend to approach a constant value of ~10wt%. The value of 7wt% can be converted to $x = 3$ in $Li_xV_2O_5{\cdot}2.4H_2O$, and it may be an upper limit for this preparation. These results are probably related to the phases of the products, as revealed in the following XRD measurements.

Figure 4 shows the XRD profiles of the Li-V oxides with various additional lithium content x's in $Li_xV_2O_5{\cdot}2.4H_2O$, prepared by heat-treatment at 120 °C. It is clarified that the β and γ phases can be prepared with an increase in the additional lithium content x ($2 \leq x \leq 3.5$). Moreover, it is worth noting that the γ phase can be obtained as almost a single phase. When the additional lithium x is over 3.5, Li-V^V oxides such as $LiVO_3$ and Li_3VO_4 can be observed to appear. Furthermore, for the β and γ phases, all the *d*-values of Bragg reflections are found to be larger compared with those of the powder specimen previously reported, indicating a lattice expansion. For example, the *d*-value of the (002) reflection for the γ phase can be found to be 0.544 nm, whereas it is 0.533 nm in the previous report [12]. Unfortunately, however, production of the ω phase can not be confirmed.

The varieties of the products in this study are very similar to those of the products obtained by a solid state reaction of Li_2CO_3 with V_2O_5, etc [8]. In general, a high temperature above 600 °C is required for the solid state

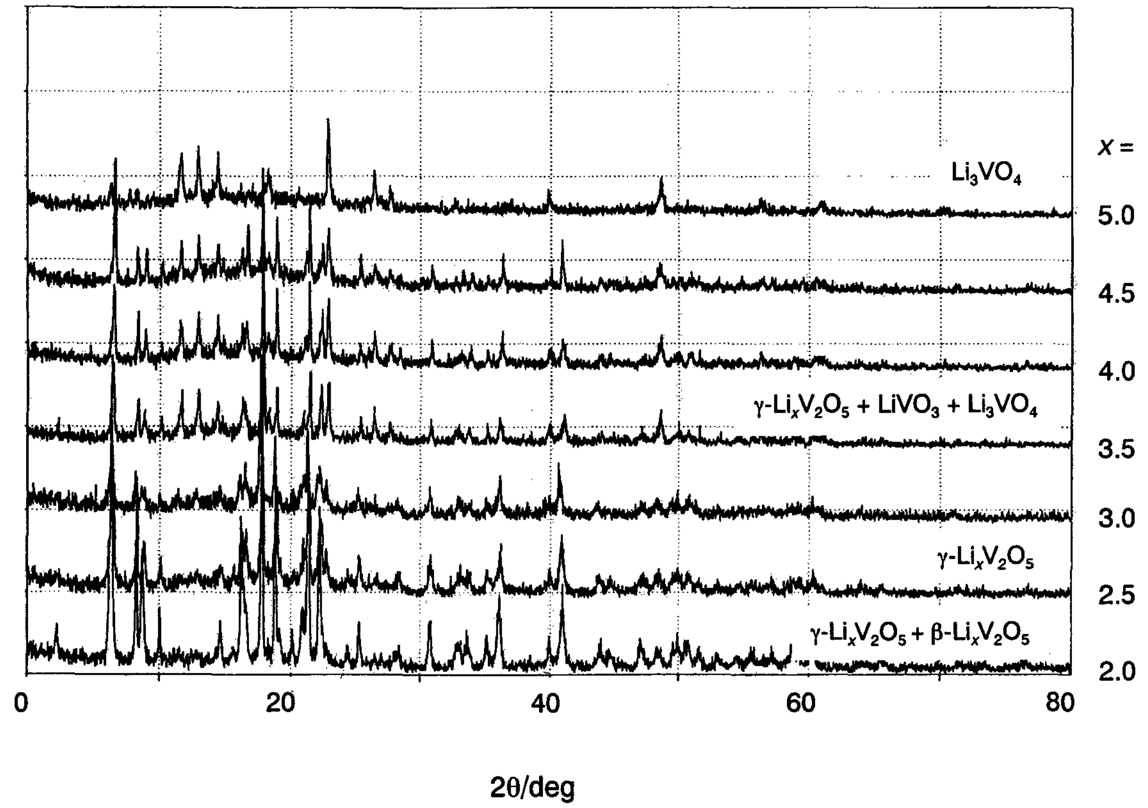

Figure 4. XRD profiles of the Li-V oxides with various additional lithium content *x*'s in $Li_xV_2O_5 \cdot 2.4H_2O$, prepared by the heat-treatment at 120 °C.

reaction, whereas in this study, the Li-V oxides can be prepared at a a significantly lower temperature such as 120 °C. The enhancement of *d*-values observed in Fig. 4 is most likely the result of the intercalation of water molecules, and such water molecules affect the electrochemical properties, as noted below.

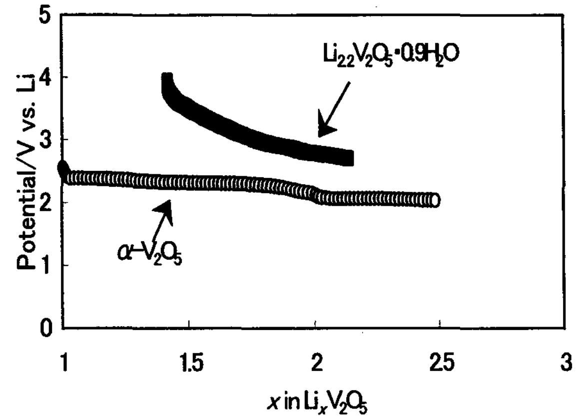

Figure 5. Charge curve for $Li_{2.2}V_2O_5 \cdot 0.9H_2O$ prepared by heat-treatment at 300 °C under an Ar atmosphere, together with the discharge curve of α-V_2O_5 [13].

Figure 5 shows the charge curve for $Li_{2.2}V_2O_5 \cdot 0.9H_2O$, together with the discharge curve of α-V_2O_5 for comparison [13]. As shown in Fig. 5, in the discharge curve of α-V_2O_5, there are two abrupt drops due to the phase transitions; the drops at x = ~1 and ~2 correspond to the δ → γ and γ → ξ transitions, respectively [7]. On the other hand, the potential of $Li_{2.2}V_2O_5 \cdot 0.9H_2O$ continuously increases with a decrease in the lithium content x. This result suggests that the material of $Li_{2.2}V_2O_5 \cdot 0.9H_2O$ is an intermediate between the amorphous and crystalline compounds [3]. Moreover, it should be noted that the potential of $Li_{2.2}V_2O_5 \cdot 0.9H_2O$ is at least 1 V higher than that of α-V_2O_5. The water of crystallization is likely to play a part in this result. However, further experiments are needed to fully understand this behavior.

4. CONCLUSIONS

We have demonstrated a new preparation method, characterization, and lithium discharge properties of the Li-V oxides. It is found that the α, β, and γ phases having the general formula of $Li_xV_2O_5$ can be prepared by reacting an aqueous H_2O_2 solution with lithium and vanadium alkoxides. Particularly, the γ phase is characteristically obtained as a single phase. By measuring the lithium charge properties, it has been found that the obtained γ phase has a high potential and a smooth charge curve.

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