Preparation and lithium insertion property of layered $Li_xV_2O_5 \cdot nH_2O$

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Abstract

Lithium vanadium oxides have been prepared by the direct reaction of an aqueous hydrogen peroxide solution with lithium and vanadium alkoxides, LiO-n-C_3H_7 and $VO(O$-i-$C_3H_7)_3$. The γ-like phase oxide can be obtained at the nominal lithium content $x_n = 3$ almost as a single phase. From the thermogravimetric (TG) measurement, it was revealed that the γ-like phase oxide contained water and organic compounds, and the water content n in $Li_xV_2O_5 \cdot nH_2O$ was found to be about 2.4 for γ-like phase oxide. Water content of the γ-like phase oxides, controlled by heat-treatment at various temperatures, affects charge and discharge behaviours markedly. It should be noted that the average potential of $Li_{2.2}V_2O_5 \cdot nH_2O$ is at least 1 V higher than that of γ-LiV_2O_5.
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1. Introduction

V_2O_5 with a layered structure is of interest as an insertion cathode material for lithium secondary batteries. The crystal structure of lithium inserted $Li_xV_2O_5$ changes from α- though ε- to δ-form reversibly upon lithium insertion up to $x = 1$, where as the structural change to γ-form occurs irreversibly. The γ-form changes finally to the ω-form at $x = 3$. These phases, except for the ω phase, primarily have two-dimensional layered structures, whereas the ω phase is considered to have a cubic rocksalt-type structure [1]. It is widely known that the ω phase has extraordinarily large charge and discharge capacities.

However, at present, the ω phase oxide can only be obtained by limited techniques such as electrochemical and chemical lithium intercalation. Moreover, these techniques are unsuitable for large-scale preparation with no impurities. From this point of view, we have initiated a study to prepare the ω phase oxide directly 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 lithium vanadium oxides using this preparation method [2].

In this study, we first demonstrate the preparation of lithium vanadium oxides and then the electrochemical properties of the obtained γ-like phase oxide.

2. Experimental

Lithium vanadium oxides were prepared by the reaction of an aqueous H_2O_2 solution with the lithium and vanadium alkoxides, LiO-n-C_3H_7 and $VO(O$-i-$C_3H_7)_3$ [3]. LiO-n-C_3H_7 and $VO(O$-i-$C_3H_7)_3$ were proportionally weighed for values of $x_n = 0-4$ with an interval of 0.5, $x_n = Li/2V$, defined as the nominal lithium content in the preparation mixture. Each weighed 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 $\sim$100 °C for 3 h. Subsequently, the excess H_2O_2 in the mixtures was decomposed with immersed platinum foils, and the organic residue was removed by extraction with diethylether. Finally, the mixtures were filtered off and dried at 120 °C to produce the lithium vanadium oxide powders.

X-ray diffraction (XRD) measurements were carried out to evaluate the crystal structures and thermogravimetric and differential thermal analyses (TG-DTA) were performed under an argon atmosphere to determine the water contents of the products. In addition, the lithium contents of the

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products were determined using an atomic absorption spectrometric method, and designated as $x = Li/2V$.

Working electrodes were prepared by mixing the oxide powders with 10 wt.% acetylene black (AB) and 10 wt.% poly-vinylidene fluoride (PVDF) in *n*-methyl pyrrolidone (NMP) solution. The mixture was spread on an aluminium foil. The composite electrodes were dried under vacuum at 150 °C for 30 min. A electrochemical cell was employed for electrochemical measurements in which lithium foil was used for a counter electrode. The electrolyte used was 1 mol dm^{-3} LiPF$_6$ in a mixture of 30 vol.% ethylene carbonate (EC) and 70 vol.% dimethyl carbonate (DMC). This cell was prepared in an argon atmosphere. Electrochemical measurements were carried out in two-electrode cells at a current density of ± 50 μA cm^{-2}.

3. Results and discussion

Fig. 1 shows the XRD patterns of the lithium vanadium oxides with various nominal lithium contents, x_n, prepared by heat-treatment at 120 °C. Lithium content obtained by the atomic absorption analysis was also presented in this figure. Details of the relation between x_n and x was described in [2]. In the XRD pattern of $x_n = 2.0$, the diffraction line found at $2\theta = 12.26°$ ($d = 7.219$) was the strongest peak of β-Li$_x$V$_2$O$_5$. It is found that the β- and γ-like layered oxide phases can be prepared within $2.0 \leq x_n \leq 3.5$. Moreover, the γ-like phase oxide can be obtained at $x_n = 3.0$ almost as a single phase. In the region of $3.5 \leq x_n \leq 5.0$, lithium vanadium oxides such as LiVO$_3$ and Li$_3$VO$_4$ can be observed. Unfortunately, however, the formation of ω phase
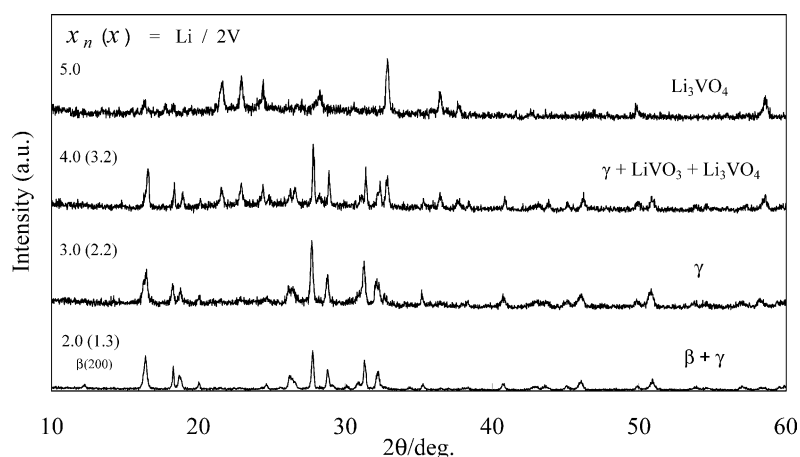

Fig. 1. XRD patterns of the samples with various x_n: nominal, and x: analytical values of lithium content Li/2V.
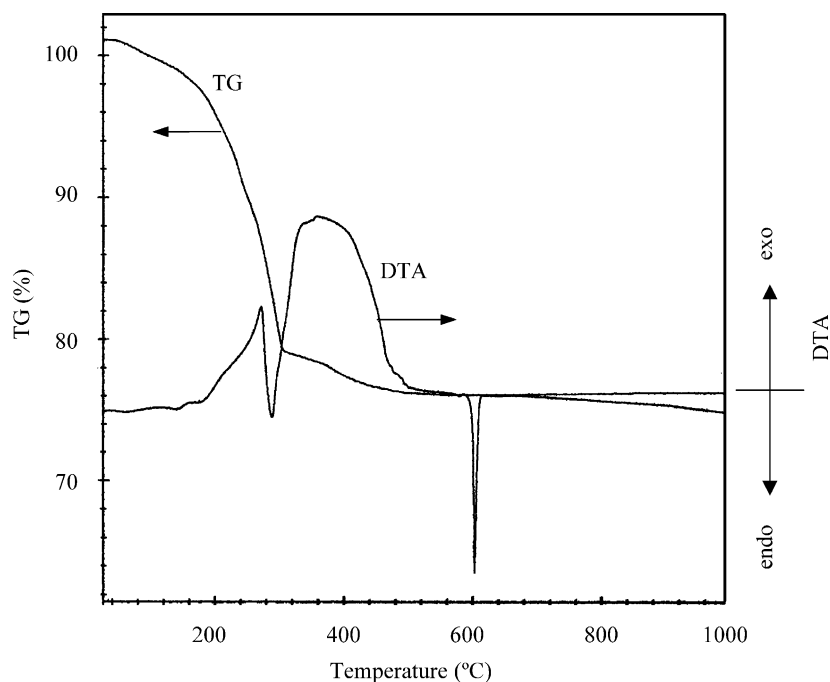

Fig. 2. TG-DTA curves for the γ-like phase oxide obtained by heat-treatment at 120 °C under Ar atmosphere.

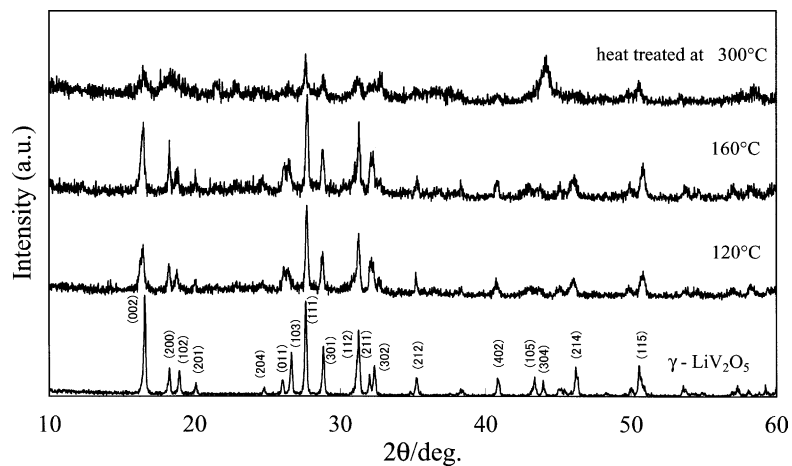Fig. 3. XRD patterns of $Li_{2.2}V_2O_5 \cdot nH_2O$.
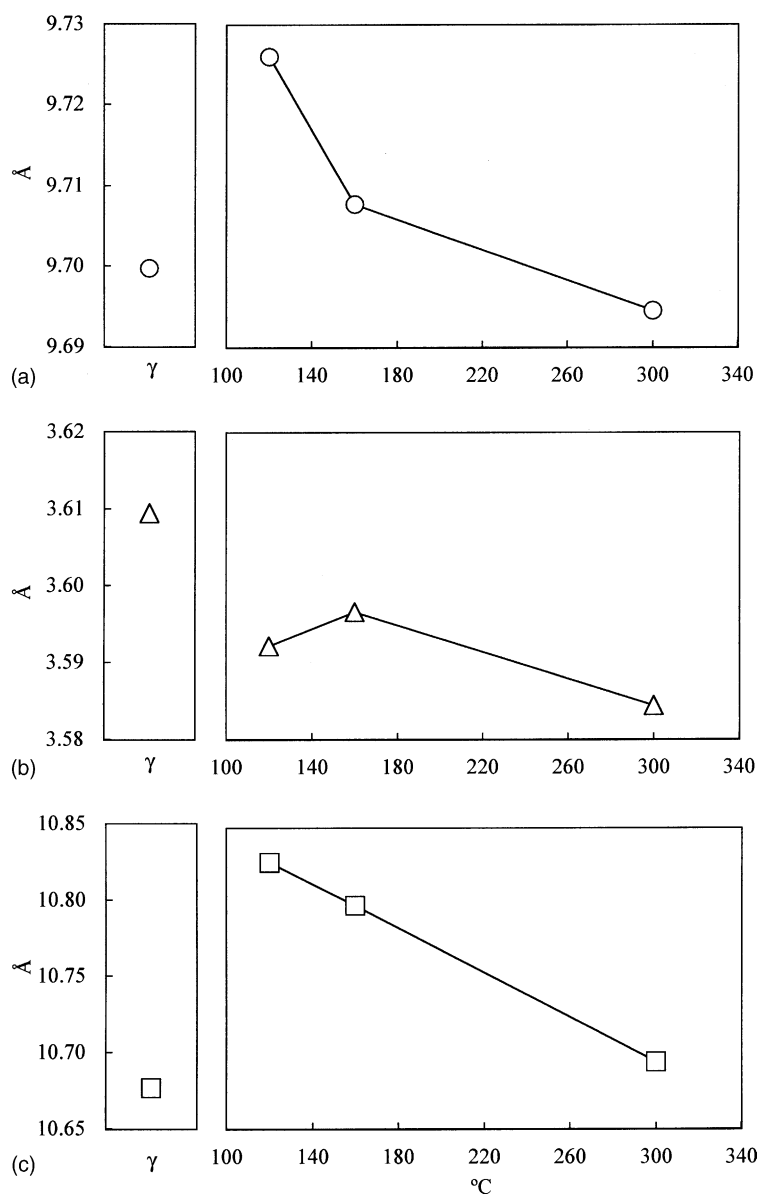

Fig. 4. Lattice parameters for $Li_{2.2}V_2O_5 \cdot nH_2O$.

can not be confirmed. In general, a high temperature above 600 °C is required for the solid state reaction, whereas in this study, the lithium vanadium oxides can be prepared at a significantly lower temperature such as 120 °C.

The lithium content of the single phase oxide with γ-like structure was found to be $x = \text{Li}/2\text{V} = 2.2$. The result of X-ray diffraction suggests that this γ-like phase oxide presumably has a layered V_2O_5 unit with lithium ions in its interlayer space, and the composition may be written as $\text{Li}_xV_2O_5$, though the oxidation state of vanadium must be examined further.

Fig. 2 shows typical TG-DTA curves for the γ-like phase oxide 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 RT $\sim$ 300 °C, which is considered to correspond to the release of water in the crystal. A weight loss of about 3% in the region of 300–450 °C with large exothermic curve may be due to decomposition of the organic compounds. From the TG measurement, it was revealed that the γ-like phase oxide contained water and organic compounds, and the water content $n = \text{H}_2\text{O}/\text{Li}_xV_2O_5$ was found to be approximately 2.4 for γ-like phase oxide. Furthermore from the results of the atomic absorption spectrometry method, the lithium content x in $\text{Li}_xV_2O_5 \cdot n\text{H}_2\text{O}$ was estimated to be 2.2 for γ-like phase oxide, and water molecules presumably exist in the interlayer space.

In order to investigate the effect of the water content on the charge and discharge properties, three kinds of samples, of heat-treated γ-like phase oxides at 120, 160 and 300 °C under an argon atmosphere were prepared. Fig. 3 shows XRD patterns for the samples of heat-treated $\text{Li}_{2.2}V_2O_5 \cdot n\text{H}_2\text{O}$ (γ-like phase oxide) at 120, 160 and 300 °C under argon atmosphere, together with XRD pattern of γ-LiV_2O_5 prepared by the solid state reaction for comparison. The heat-treated γ-like oxide is stable up to 160 °C, but the crystallinity of the heat-treated γ-like phase oxide is low compared with γ-like phase oxide. At 300 °C, where almost all water in the oxide releases, γ-like phase oxides tends to be amorphous. A new diffraction line is found at $2\theta = 44.16°$ ($d = 2.05$). Lattice parameters (see Fig. 4), especially of the c-axis, tend to decrease, and crystallinity tend to decrease, as the heat treating temperature increases. This may be a results of release of water from the layered structure.

Fig. 5 shows the charge and discharge (extraction and insertion) curves for $\text{Li}_{2.2}V_2O_5 \cdot n\text{H}_2\text{O}$ (γ-like phase oxide), together with the discharge curve of γ-LiV_2O_5 for comparison. The water content of the γ-like phase oxides, controlled by heat-treatment at various temperatures, affects the charge and discharge behaviours markedly. It was found that the extraction and insertion processes occurred in two main steps for heat-treated sample at 120 °C. As the heat-treatment
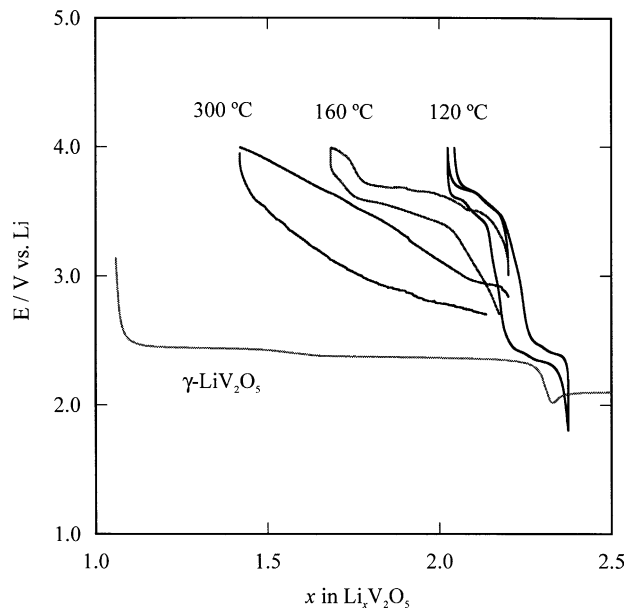

Fig. 5. Charge and discharge curves of $\text{Li}_{2.2}V_2O_5 \cdot n\text{H}_2\text{O}$, together with the discharge curve of γ-LiV_2O_5.

temperature rose, the plateaus became longer (at 160 °C) and further became featureless, typical of amorphous oxides (at 300 °C). The lithium extraction–insertion capacity was 0.8 mol in the heat-treated sample at 300 °C, and the lithium extraction–insertion capacity became larger as the content of water decreased. Moreover, it should be noted that the average potential of γ-like phase oxides is at least 1 V higher than that of γ-LiV_2O_5.

4. Conclusion

Layered γ-like phase oxides were prepared as single-phases by the sol–gel method with alkoxide lithium and vanadium hydrogen peroxide, at low temperatures, compared with conventional high temperature solid state reactions. The γ-like phase contains water and organic compounds. The lithium extraction–insertion capacities of the γ-like phase oxides were smaller, but had higher average potentials. The water content of γ-like phase oxides was decreased by a heat-treatment, but the lithium extraction–insertion capacity increased.

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