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Low-temperature preparation of lithium vanadium oxides by solution processing

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Abstract

Lithium vanadium (Li–V) oxides were prepared by solution processing using the reaction of an aqueous hydrogen peroxide solution with lithium and vanadium alkoxides, LiO-*n*-C_3H_7 and VO(O-*i*-$C_3H_7)_3$. It was found that various phases of the Li–V oxides such as the orthorhombic 2D-V_2O_5 compound, and the β- and γ-phases having the general formula of $Li_xV_2O_5$ ($0 \leqslant x < 2.2$) are obtained at low temperature such as ~300 °C. Particularly, it should be noted that γ-$Li_xV_2O_5$ can be prepared as a single phase in the x range of 1.3–2.2. The charge and discharge behavior for the γ-phase material ($x = 2.2$) is discussed as compared to that of the γ-phase material ($x = 1$) prepared by conventional high temperature solid-state reaction.

Keywords: Charge and discharge behavior; Lithium and vanadium oxides; γ-$Li_xV_2O_5$; Solution processing

1. Introduction

Vanadium oxide (α-V_2O_5) is of interest as a promising candidate for the positive electrode material of lithium secondary batteries.[1] During the electrochemical lithium intercalation process, α-V_2O_5 changes into several different phases; the α-, ε-, δ- and γ-phases with the general formula of $Li_xV_2O_5$ successively appear as the lithium content x increases up to $x = 1$.[2] These phases primarily have a two-dimensional layered structure as well as the α-V_2O_5 compound.[3] Moreover, C. Delmas et al.[1] reported that the γ-phase changes to the ω-phase at $x = 3$, which is considered to have a cubic rocksalt-type structure. Such γ- and ω-phases are of particularly interest, for they have large charge and discharge capacities without almost structural modification even at a low voltage.[1,4]

It is known that the above Li–V compounds can be prepared by electrochemical or chemical lithium intercalation, or a solid-state reaction.[1–5] However, these methods are not suitable for large-scale preparation with no impurities. On the other hand, solution processing is a useful technique for producing various kinds of metal oxides under mild conditions, such as low temperature and atmospheric pressure.[6] In addition, there is the advantage that the particle size can be controlled relatively easily.[5,7]

In this paper, we first describe the preparation of the lithium vanadium oxides using solution processing, then the characterization results of the obtained materials. Second, the charge and discharge properties (lithium extraction and insertion properties) for the γ-phase material ($x = 2.2$) are briefly discussed as compared to that of the γ-phase material prepared by conventional high temperature solid-state reaction.

2. Experimental

The 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*-$C_3H_7)_3$.[8] Each alkoxide was proportionally weighted for values of $x = 0$–5 in terms of $Li_xV_2O_5$, then dissolved in a small amount of 2-ethoxyethanol ($C_2H_5OC_2H_4OH$). These mixtures were added in limited amounts of an aqueous 15% H_2O_2 solution, then refluxed at ~100 °C for 3 h. Subsequently, the excess H_2O_2 in the solutions was decomposed using a Pt net, and the organic residue was removed by extraction with diethyl ether. Finally, the solutions was filtered off and dried in air at 120 °C to produce the lithium vanadium oxides.

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In order to investigate the water content and impurity phases in the as-prepared Li–V oxides at 120 °C, thermogravimetry (TG) coupled with mass spectroscopy (MS) measurements were carried out using a Rigaku thermo-mass system. The phases were determined by powder X-ray diffraction measurements using a Jeol JDX3500 diffractometer. In addition, the lithium content in the Li–V oxides heat-treated at 500 °C in an argon atmosphere was evaluated by atomic adsorption spectrometry analyses.

The charge and discharge behavior was investigated for the γ-phase compound ($x=2.2$) prepared by the heat-treatment at the temperature of 300 °C in an argon atmosphere, using a two-electrode cell equipped with a lithium foil as the counter electrode. The working electrode was prepared as follows. A mixture of the γ-phase material, 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, then dried under vacuum at 150 °C for 30 min. A solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate with a volume ratio of 3:7 was used for the electrolyte. The charge and discharge measurements were performed at a current density of ± 50 μA cm^{-2}.

3. Results and discussion

Fig. 1 shows the relationship between the analytical and additional lithium quantities. It was found that the analytical values are almost identical with the additional ones up to ~7 wt.%, and then tend to approach a constant value of ~11 wt.%. The values of ~7 and ~11 wt.% correspond to $x=\sim 2$ and $x=\sim 3.3$ in terms of $Li_xV_2O_5$, respectively. Such behavior usually happens for the preparation using solution processing.[6]

Fig. 2 shows the TG curve for the Li–V oxide ($x=2.2$) obtained at 120 °C. The measurement was done in an argon atmosphere at the heating rate of 5 °C. Note that the x values refer to the estimated ones based on the chemical analyses, hereafter. During the heating process from room temperate to ~500 °C, TG weight losses occur approximately in four temperature regions; room temperature–180, 180–300, 300–420 and 420–500 °C, and the total TG weight loss can be estimated to be 24 wt.%. From the MS measurements, it was found that the chemical species produced in each TG region are H_2O, CO_2 or organic compounds (probably corresponding to the materials derived from 2-ethoxyethanol). These results are summarized in Table 1. The empirical formula of the Li–V oxide ($x=2.2$) at room temperature is taken as $Li_{2.2}V_2O_5 2.89H_2O 0.05CO_2$, except for the organic compounds.

Fig. 3 shows the XRD profiles for the Li–V oxides obtained at 120 °C with various x values of 0–3.2 in terms of $Li_xV_2O_5$. It was found that 2D-V_2O_5, β- and γ-$Li_xV_2O_5$, and Li_3VO_4 characteristically occur according to the variation in the lithium content. Table 2 lists the relationship between the x value region and the corresponding as-prepared Li–V phases at 120 °C. The 2D-V_2O_5 compound was first prepared from the reaction of vanadium metal powder with an aqueous H_2O_2 solution by M. Hibino et al.[9] and they reported that this compound takes a random layer lattice structure based on the *a–b* plane of orthorhombic V_2O_5. In addition, for lithium intercalation processes the heat-treatment at the

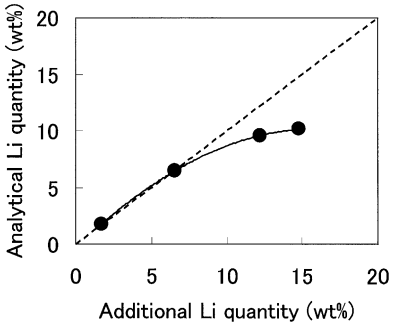

Fig. 1. The relationship between the additional and analytical quantities.

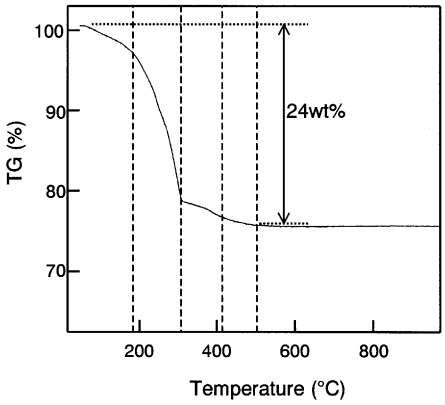

Fig. 2. TG curve for the Li–V oxide ($x=2.2$) obtained at 120 °C. The measurement was done in an argon atmosphere at the heating rate of 5 °C. The TG weight loss occurred approximately in four temperature regions; room temperature–180, 180–300, 300–420 and 420–500 °C.

Table 1
Each TG weight loss and the corresponding principal species produced during the heat-treatment of the Li–V oxide ($x=2.2$) in the temperature range of 120–500 °C and in an argon atmosphere

Temperature (°C)	TG weight loss (%)	Principal species
RT–180	2.8	H_2O
180–300	18	H_2O
300–420	2.1	CO_2
420–500	<1.1	Organic compounds

From these results, the empirical formula except for the organic compounds is taken as $Li_{2.2}V_2O_5 2.89H_2O 0.05CO_2$ at room temperature.

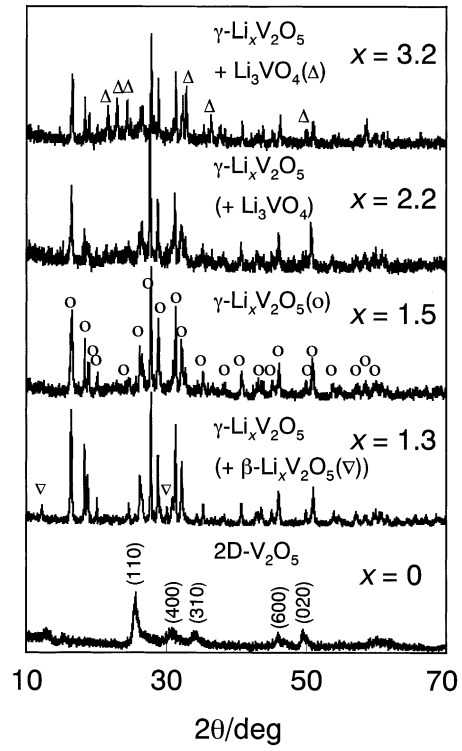

Fig. 3. The XRD profiles of the Li–V oxides obtained at 120 °C with various x values of 0–3.2 in terms of $Li_xV_2O_5$.

temperature of above 400 °C is usually needed to obtain the β- and γ-phases,[2] whereas theses phases occur at considerably low temperature such as 120 °C in this study. Unfortunately, however, the preparation of the ω-phase can not been confirmed in this study.

Fig. 4 illustrates the charge and discharge curves for the γ-phase material ($x = 2.2$) heat-treated at the temperature of 300 °C in an argon atmosphere, together with the discharge curve of the γ-phase material prepared by a solid-state reaction of $LiVO_3$ with VO_2 at 600 °C, for comparison.[5] Note that the material in this study contains a small amount of CO_2 and organic compounds as mentioned above. It can be seen in Fig. 4 that the potential of the γ-phase material in this study continuously varies with almost no plateaus during both charge and discharge processes, and its discharge potentials are at least 0.5 V higher than that of the comparison sample. The former fact suggests that the material is an intermediate between the amorphous and crystalline compounds.[9] The latter might be related to the structure and/or impurity phases. Somehow, it should be pointed out that these facts are favorable for the positive electrode material of lithium secondary batteries. However, it was found that the discharge capacity is smaller than that of the comparison sample. Further investigations are needed to fully understand the electrochemical properties of the materials.

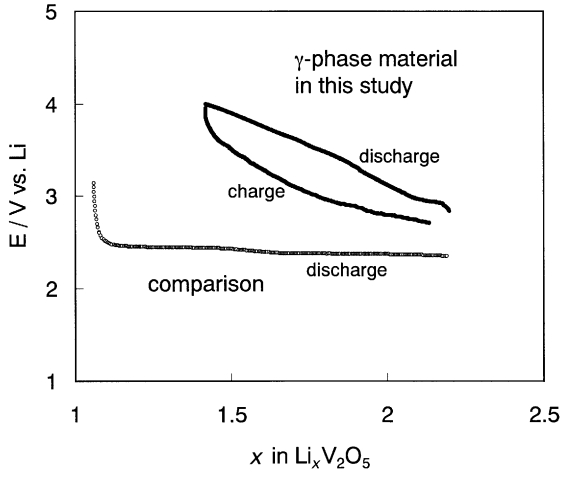

Fig. 4. Charge and discharge curves of the γ-phase material ($x = 2.2$) prepared by the heat-treatment at the temperature of 300 °C in an argon atmosphere, together with the discharge curve of the γ-phase material prepared by a solid state reaction, for comparison.

Table 2
The relationship between the x value region and the corresponding phases at 120 °C

X	Phases
0–0.5	2D-V_2O_5
0.5–1	2D-V_2O_5 + β-$Li_xV_2O_5$
1–1.3	γ-$Li_xV_2O_5$ + β-$Li_xV_2O_5$
1.3–2.2	γ-$Li_xV_2O_5$
2.2–	γ-$Li_xV_2O_5$ + Li_3VO_4

4. Conclusions

We have demonstrated the preparation of Li–V oxides by solution processing using the reaction lithium and vanadium alkoxides with an aqueous H_2O_2 solution. In this preparation processing, several different phases of Li–V oxides, containing a large amount of water molecule and a small amount of CO_2 and organic compounds, occur at considerably low temperature such as 120 °C. It is found that such water molecules can be removed by heat-treatment at the temperature of 300 °C. In addition, it should be noted that γ-$Li_xV_2O_5$ ($1.3 < x < 2.2$) can be prepared as a single phase. The γ-$Li_{2.2}V_2O_5$ compound shows some favorable charge and discharge properties. At present, further investigations are in progress to clarify the properties.

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