

Sol-gel preparation of Li-V oxides
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Li-V oxides have been prepared by reacting an aqueous H₂O₂ solution with Li and V alkoxides (LiO-*n*-C₃H₇ and VO(O-*i*-C₃H₇)₃) at ~100 °C. The α-V₂O₅, β-LiV₂O₅, γ-LiV₂O₅, LiVO₃, and Li₃VO₄ phases having ~18%H₂O respectively appear with the lithium content. Electrochemical insertion and deinsertion behaviors of lithium ion in the anhydrous compounds prepared by a heat-treatment at 300 °C are discussed.

It is well known that orthorhombic V₂O₅ has a layered structure and is of interest as an insertion cathode material for lithium secondary batteries [1]. Various phases appear with the electrochemical insertion of lithium ion in V₂O₅; the α-, ε-, and δ-phases form reversibly up to $x = \sim 1$ for Li_{*x*}V₂O₅, and the γ-phase forms irreversibly above $x = 1$. Further the γ-phase changes to the ω-phase at $x = \sim 3$ [2]. Structurally, the α-, ε-, δ-, and γ-phases exhibit an orthorhombic layered form, while it is reported that the ω-phase (Li₃V₂O₅) have a cubic rock-salt form [2]. In addition, the ω-Li₃V₂O₅ material is considered to have an advantage of permitting a high specific energy and a stability at low voltage without structure modification [2].

Numerous works were devoted to vanadium bronzes (M_{*x*}V₂O₅; M = Li, Na, K, Cu, etc.). To our knowledge, however, the direct preparation of the γ- and ω-phases has been reported only a few papers [3].

Sol-gel preparation is a useful technique for producing fine particles of a variety of materials under mild conditions, such as low temperature and atmospheric pressure. Recently we have also succeeded in preparation of γ-LiV₂O₅ with a pure phase by a sol-gel method. In this study, it is demonstrated the preparation for the first time. In addition, the electrochemical insertion and deinsertion behaviors of lithium ion in the anhydrous compounds are discussed.

Li-V oxides were prepared by the direct reaction of an aqueous H₂O₂ solution with LiO-*n*-C₃H₇ and VO(O-*i*-C₃H₇)₃ [4]. LiO-*n*-C₃H₇ was weighted proportionally for composition of $x = 0 - 5$ in Li_{*x*}V₂O₅. Every weighted quantities of LiO-*n*-C₃H₇ was dissolved in limited amounts of 2-ethoxyethanol, and mixed VO(O-*i*-C₃H₇)₃. The mixtures were cooled by ice water, and added in 30 -100 ml of an aqueous H₂O₂ solution by stirring. Subsequently, the mixtures were refluxed at ~100 °C for 3 h, and the excess H₂O₂ in the solutions was catalytically decomposed using several platinum foils. Finally, the solutions were dried by evaporation at 120 °C to produce Li-V oxide powders.

X-ray diffraction (XRD) measurements and thermogravimetric and differential thermal analysis (TG-DTA) were carried out to determine the phases and the water content of the as-precipitated powders.

XRD reveals that α-V₂O₅, β-LiV₂O₅, γ-LiV₂O₅, LiVO₃, and Li₃VO₄ appears successively in the as-precipitated materials according to an increase in the lithium content. Table 1 shows the summary of phases and compounds isolated for various lithium contents *x*. The *x* values in table 1 are estimated from the amounts of added LiO-*n*-C₃H₇. It is observed that the β-LiV₂O₅ phase is observed for $x = 2$. The β-phase is considered to be made by a high temperature (above 400 °C) for the preparation using a solid state reaction [3]. Moreover, it should be noted that the γ-LiV₂O₅ phase can be prepared in the *x* range of 2.5 – 3.0, in a pure phase.

On the other hand, TG-DTA reveals that every as-precipitated material has ~18%H₂O, which may exists

in a layered structure. Thus, for the γ-phase, its chemical formula can be represented as LiV₂O₅· 2.5H₂O. However, such water of crystallization is found to be removed by a heat-treatment at ~300 °C.

Electrochemical insertion and deinsertion behaviors of lithium ion in the anhydrous compounds will be discussed.

References

1. M. Eguchi, F. Maki, H. Kimura, K. Takahashi, and Y. Momose, *Electrochemistry*, **68**, 474 (2000).
2. C. Delmas, H. Cognac-Auradou, J. M. Cocciantelli, M. Ménétrier, and J. P. Doumerc, *Solid State Ionics*, **69**, 257 (1994).
3. P. Rozier, J. M. Savariault, and J. Galy, *Solid State Ionics*, **98**, 133 (1997).
4. K. Tatsumi, M. Hibino, and T. Kudo, *Solid State Ionics*, **96**, 35 (1997).

Table 1
 Summary of phases and compounds obtained at 120 °C for various amounts in lithium

<i>x</i> in Li _{<i>x</i>} V ₂ O ₅	compounds and phases
0 – 1.5	α-LiV ₂ O ₅
2	β-LiV ₂ O ₅ , γ-LiV ₂ O ₅
2.5 – 3.0	γ-LiV ₂ O ₅
3.5 – 4.5	γ-LiV ₂ O ₅ , LiVO ₃ , Li ₃ VO ₄
5.0	LiVO ₃