

Preparation and lithium insertion behaviour of oxygen-deficient $\text{Li}_{1+x}\text{V}_3\text{O}_{8-\delta}$

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Received 17 September 1996; accepted 21 October 1996

Abstract

Oxygen deficient $\text{Li}_{1+x}\text{V}_3\text{O}_{8-\delta}$ ($0.03 < \delta < 0.2$) is prepared by reduction of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ with carbon. From infrared spectroscopic (IR) studies, it is found that specific oxygen is removed from the host lattice. Electrochemical measurement reveals that more lithium is inserted in $\text{Li}_{1+x}\text{V}_3\text{O}_{8-\delta}$ compared with original $\text{Li}_{1+x}\text{V}_3\text{O}_8$ contrary to a decrease in pentavalent vanadium V(V) by the introduction of oxygen defects. This is probably due to the formation of new sites available for the occupation of Li^+ ions. During the oxidation process by charging of $\text{Li}_{1+x}\text{V}_3\text{O}_{8-\delta}$ containing V(IV), Li^+ ions are extracted from the octahedral sites and inserted at the initial stage of discharge process. These effects result in an increase in the total amount of inserted lithium.

Keywords: Lithium; Vanadium; Oxygen; Deficiency; Insertion

1. Introduction

Lithium vanadate $\text{Li}_{1+x}\text{V}_3\text{O}_8$ with the layered structure is considered to be a promising positive electrode material for lithium secondary batteries. The main advantage is that the material can accommodate up to three equivalent lithium per formula unit. Vanadium exists in a pentavalent state though Li(I) is contained in the host structure before discharge. A good cycling performance is derived from the fact that the layers composed of V_3O_8^- are linked strongly by an ionic bond between Li(I) ions and octahedrally coordinated oxygen atoms faced to the layers, and that the host structure changes little on lithium insertion and extraction [1].

The authors investigated the effects of substitution of Mn(IV) or Mo(VI) for a part of V(V) in the layer on the crystal structure and on the electrochemical insertion behaviour [2]. It was revealed that the limit of lithium insertion depended on the number of sites for occupation by Li(I) ions rather than the oxidation state of vanadium.

In this paper, a description is given of the effects of introducing oxygen defects in the host lattice on the lithium insertion behaviour of $\text{Li}_{1+x}\text{V}_3\text{O}_{8-\delta}$.

2. Experimental

$\text{Li}_{1.2}\text{V}_3\text{O}_8$ as the starting material was synthesized as described previously [2]. A mixture of Li_2CO_3 (Yoneyama Chemical Industries, >99.0%) and V_2O_5 obtained by decomposition of NH_4VO_3 (Soekawa Chemicals, >99%) at 500 °C for 24 h was melted in a molar ratio of 1.2:3 at 680 °C for 24 h in air, and then cooled slowly to room temperature. Atomic absorption analysis was carried out to determine the lithium content of the sample. The content of tetravalent vanadium V(IV) that existed previously in the starting material was determined by the redox titration technique suggested by Wickham [3], and the composition was found to be $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$.

Oxygen defects were introduced into the crystal lattice by reduction of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$ with carbon. After mixing the powdered sample sieved under 38 μm with acetylene black (carbon, Denka black, Denkikagaku Kogyo) in the appropriate ratio, the oxygen defect was $\delta = 0.1\text{--}0.5$ in $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$. A pellet with a diameter of 1.0 cm was obtained by pressing the mixture under $2 \times 10^4 \text{ N cm}^{-2}$ in the die (Ninomiya shoji, diameter: 5.0 mm). This pellet was heated in a platinum crucible at 500 °C for 24 h under a flowing nitrogen atmosphere in the quartz tube and $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ was obtained. The content of oxygen defects (δ) in the formula $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ was determined by measuring the concentration of V(IV) by the redox titration technique mentioned above. The crystal

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structure was analysed by powder X-ray diffraction (XRD, Rigaku, RINT 1300, Cu K α radiation with Ni filter) and infrared spectroscopic (IR) methods (Bio-Rad, FTS-65).

All electrochemical measurements were performed in a cylindrical glass cell. Lithium wires (Aldrich, >99.9%, diameter: 3.2 mm) were used as the counter and reference electrodes. A 1 M LiClO₄/propylene carbonate (PC) solution (Mitsubishi Chemical, water content <20 ppm) was used as the electrolyte. Sample oxides sieved under 38 μ m, acetylene black (carbon, Denka black, Denkakagaku Kogyo) and poly(tetrafluoroethylene) were mixed in the weight ratio of 80:15:5 and pressed on a nickel porous net at 2×10^4 N cm⁻³. The resulting pellet was connected to a lead wire by silver paste on a porous nickel side of the pellet and insulated electrically with silicone resin to leave the opposite side of the pellet as the electrode surface. Galvanostatic discharge was performed at a current density of 0.1 mA cm⁻² with a potentiostat (Toho Technical Research, 2092 and PS-08). Cyclic voltammetry was performed at a scanning rate of 0.01 mV s⁻¹ with the potentiostat described above and a function generator (Hokuto Denko, HB-104).

3. Results and discussion

The XRD patterns of oxygen-deficient Li_{1.2}V₃O_{8- δ} together with that of the starting material are given in Fig. 1. While the pattern for $\delta=0.14$ was as same as that for the starting material, some peaks ascribed to β -Li_{0.30}V₂O₅ (marked by arrows) appeared for $\delta=0.22$. Changes in the lattice constants calculated from the diffraction angles obtained from XRD patterns (Fig. 1) are shown in Fig. 2. For $\delta < 0.2$, a_0 and b_0 increase linearly while the others are almost constant. These results indicate that samples with oxygen defects in the crystal lattice for $\delta < 0.2$ are obtained as a single phase.

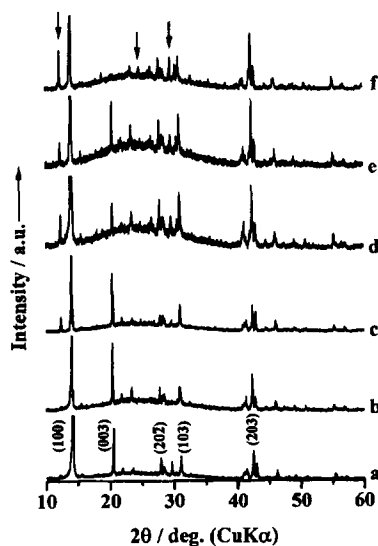


Fig. 1. XRD patterns for Li_{1.2}V₃O_{8- δ} : (a) $\delta=0.03$; (b) $\delta=0.14$; (c) $\delta=0.22$; (d) $\delta=0.25$; (e) $\delta=0.31$, and (f) $\delta=0.35$.

The IR spectra of the starting ($\delta=0.03$) and oxygen-deficient ($\delta=0.14$) samples are given in Figs. 3 and 4. It was reported [4] that the absorption bands near 1000 and 950 cm⁻¹ are associated with the stretching vibration of V(2)=O(4) and those of V(3)=O(7) and V(1)=O(5), respectively (number in parentheses represents the position of the atoms labelled by de Picciotto et al. [5], see Fig. 5). A band near 750 cm⁻¹ is ascribed to the stretching vibration of V-O-V and no remarkable change appeared in this case.

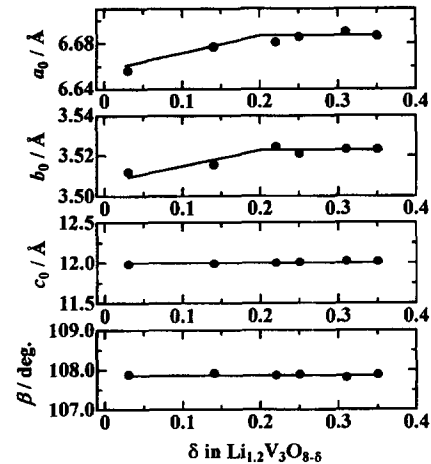


Fig. 2. Lattice parameters of Li_{1.2}V₃O_{8- δ} .

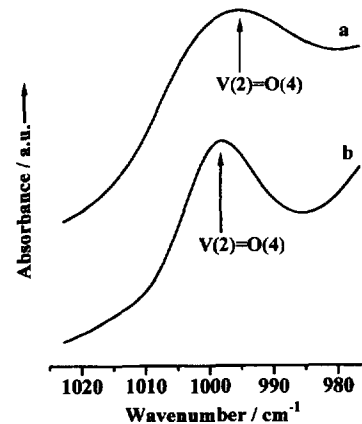


Fig. 3. IR spectra for Li_{1.2}V₃O_{8- δ} : (a) $\delta=0.14$, and (b) $\delta=0.03$ (starting material).

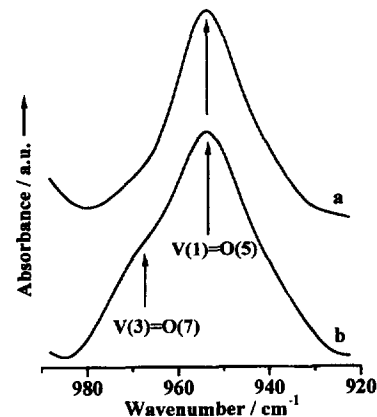


Fig. 4. IR spectra for Li_{1.2}V₃O_{8- δ} : (a) $\delta=0.14$, and (b) $\delta=0.03$.

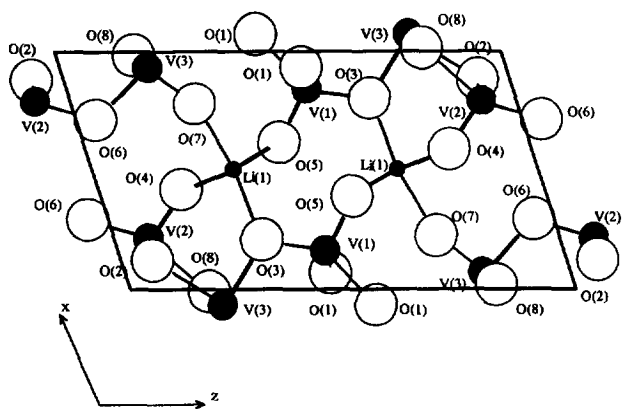


Fig. 5. View from [010] direction of the crystal structure of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ [5].

For the spectra of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$), it is observed that a band near 1000 cm^{-1} shifts to lower wave numbers from 1000 to 996 cm^{-1} (Fig. 3) and another band near 950 cm^{-1} is sharpened (by decreasing $\text{V}(3)\text{--O}(7)$ absorption band strength) without any shift at 953 cm^{-1} (Fig. 4). If $\text{O}(7)$ is removed, $\text{Li}(1)$ will pull $\text{O}(4)$ more strongly than $\text{O}(3)$ or $\text{O}(5)$ because either $\text{O}(3)$ or $\text{O}(5)$ is one of the oxygen atoms that construct the layer of VO_5 chains and $\text{O}(4)$ is a dangling oxygen faced to the layer gap. This causes a longer $\text{V}(2)\text{--O}(4)$ bond length. This assumption may explain the fact of shifting of a band near 1000 cm^{-1} to lower wave numbers and sharpening of another band near 1000 cm^{-1} .

Discharge curves of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$ ($\delta=0.03$; the starting material) and $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$) are given in Fig. 6. The shape of the curve of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$ is similar to those of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ reported in many previous papers [6–9]. But some new steps appeared on the curve of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$) and the limit of lithium insertion increases, contrary to expected from the decrease in the content of $\text{V}(\text{V})$ by introduction of oxygen defects. It has been reported that amorphous $\text{Li}_{1+x}\text{V}_3\text{O}_8$ has a larger discharge capacity than the crystalline counterpart [10]. But as the XRD pattern (see Fig. 1) indicates crystallinity to a certain extent on removal of oxygen, the increase in the insertion limit observed on the discharge curve is caused by the appearance of new available sites for Li^+ ions in the crystal structure.

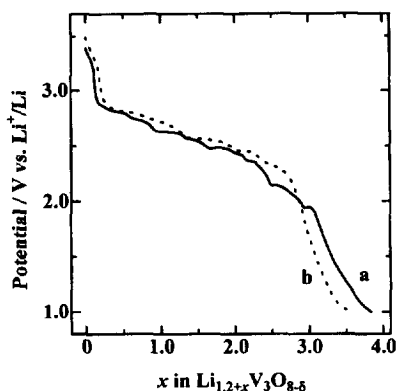


Fig. 6. Discharge curves for $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ at -0.1 mA cm^{-2} : (a) $\delta=0.14$, and (b) $\delta=0.03$.

It is expected that Li^+ ions in the octahedral sites might be extracted by electrochemical oxidation of $\text{V}(\text{IV})$ which is formed by introduction of oxygen defects. Fig. 7 presents the galvanostatic charging curves for the extraction of lithium. Compared with $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$ ($\delta=0.03$), two plateaus appear at 3.45 and 3.61 V on the curve for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$). It is already known that x in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ represents an excess of Li^+ ions, which occupy the tetrahedral sites and are able to be extracted on charging up to 3.8 V in an $\text{LiClO}_4/\text{PC-DME}$ solution [7]. Consequently, after Li^+ ions at the tetrahedral sites are extracted under 3.45 V , Li^+ ions at the octahedral sites are extracted in the potential range of about 3.6 V . The extraction process of lithium for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$, however, is not observed clearly and a relative large over-voltage on charging suggests that a side reaction, such as decomposition of the electrolyte, occurs simultaneously. The charging curves to higher potential (over 4.0 V) are shown in Fig. 8. The sharp rise of potential starting at 4.0 V is presumably due to 'passive film formation' of the oxide surface by extraction of Li^+ ions.

From the XRD pattern of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$) shown in Fig. 9, conservation of the original structure indicates that extraction of Li^+ ions takes place without structural change after charging up to 4.0 V .

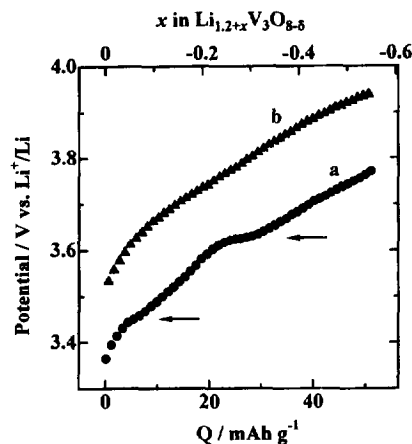


Fig. 7. Charging curves for $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ at $+0.1\text{ mA cm}^{-2}$: (a) $\delta=0.14$, and (b) $\delta=0.03$.

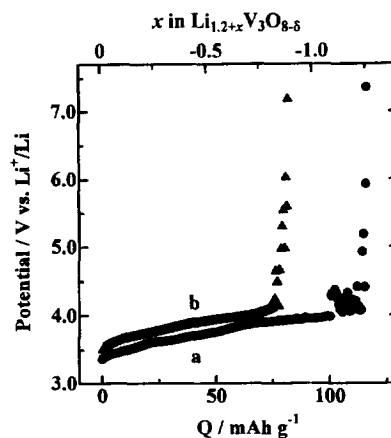


Fig. 8. Charging curves for $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ at $+0.1\text{ mA cm}^{-2}$: (a) $\delta=0.14$, and (b) $\delta=0.03$.

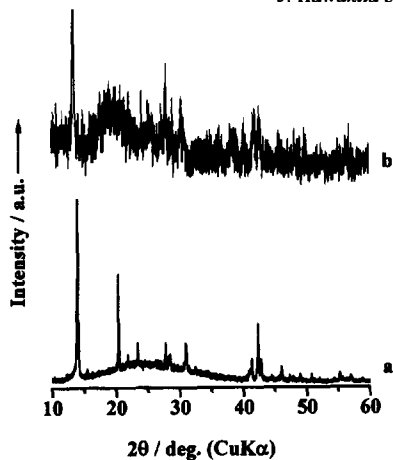


Fig. 9. XRD patterns for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$: (a) before charge, and (b) after charge up to 4.0 V.

Li^+ ions that occupy the octahedral sites of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$) are reversibly extracted on charging and are inserted at the initial stage of the discharge process, as shown in Fig. 10. As additional Li^+ ions are inserted in the low potential range around 2.0 V, the total amount of inserted lithium is larger compared with $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$.

The XRD patterns of the samples with various extents of lithium insertion $\text{Li}_{1.2+x}\text{V}_3\text{O}_{7.86}$ are given in Fig. 11. While lithium insertion proceeds, the original single-phase is retained in the range of $-0.4 < x < 1.5$ and splitting of a few peaks indicate the appearance of a new phase at $x=3.0$. At $x=4.0$, the two phases still exist and the potential drop at this stage (see Fig. 10) may be caused by a slow lithium diffusion in the second phase. Fig. 12 presents the relation between inserted lithium content (x) and the interlayer distance calculated from the XRD pattern (see Fig. 11). Contraction of the interlayer distance of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$) is larger and the interlayer distance becomes smaller than in the case of $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$. Both materials have the second phase with larger distances at about $x > 2.0$.

Cyclic voltammograms are given in Fig. 13. The profile for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.97}$ is similar to those reported by Pistoia and co-workers [8,10]. It has three cathodic peaks between 2.0 and

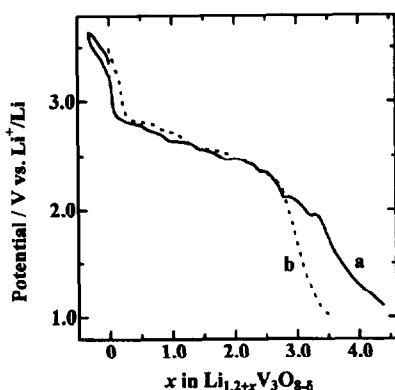


Fig. 10. Charge and discharge curves for $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ at $\pm 0.10 \text{ mA cm}^{-2}$: (a) $\delta=0.14$, and (b) $\delta=0.03$.

3.0 V that correspond to lithium insertion in sites with energy difference for holding of Li^+ ions. $\text{Li}(\text{I})$ ions at the octahedral sites might be extracted and inserted reversibly and additional cathodic and anodic peaks appeared near 3.5 V for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.86}$ ($\delta=0.14$). A new cathodic peak near 2.0 V and a new anodic one near 2.9 V are considered to be associated

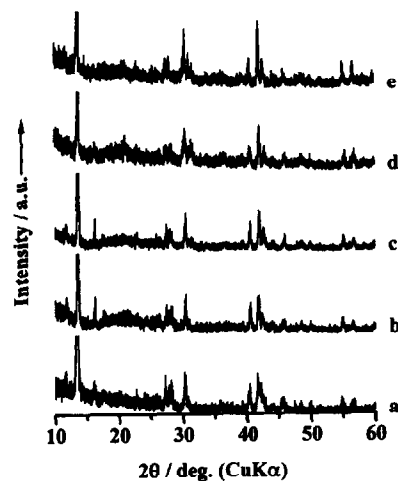


Fig. 11. XRD patterns for $\text{Li}_{1.2+x}\text{V}_3\text{O}_{7.86}$: (a) $x=-0.4$; (b) $x=0$; (c) $x=1.5$; (d) $x=3.0$, and (e) $x=4.0$.

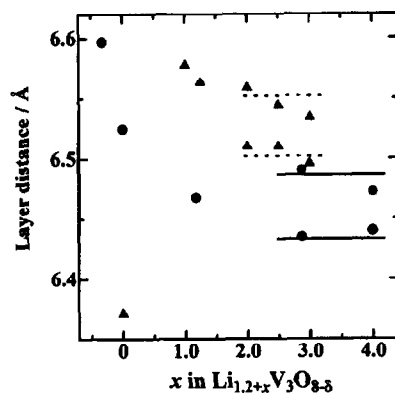


Fig. 12. Layer distance, d_{100} of $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$: (●) $\delta=0.14$, and (▲) $\delta=0.03$.

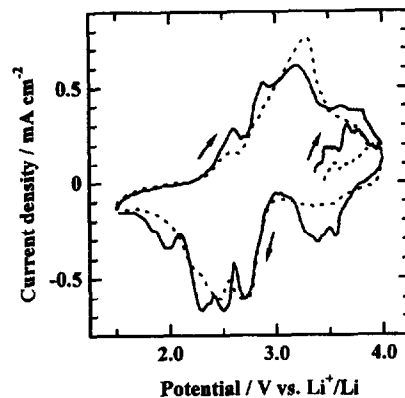


Fig. 13. Cyclic voltammograms for $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ at 0.01 mV s^{-1} : (---) $\delta=0.14$, and (···) $\delta=0.03$.

with additional lithium insertion and extraction processes, respectively. These results indicate that lithium insertion/extraction at the newly formed sites takes place with low reversibility.

4. Conclusions

Oxygen-deficient $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}$ ($0.03 < \delta < 0.2$) is obtained by reduction with carbon. Oxygen deficiency in the $\text{Li}_{1+x}\text{V}_3\text{O}_8$ structure causes reversible extraction and insertion of Li(I) ions at the octahedral sites and the formation of additional sites for insertion and extraction. These results indicate an increase in the limit of lithium insertion and extraction by the introduction of oxygen deficiency.

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