

Nanosized-Layered LiVO_2 Prepared from Peroxo-Polyvanadic Acid and Its Electrochemical Properties

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Nanosized-layered rock-salt LiVO_2 was prepared by a new method from peroxo-polyvanadic acid. The X-ray diffraction pattern was well fitted with the space group $R\bar{3}m$ in the Rietveld analysis and the crystallite size was estimated at 47 nm. The electrochemical properties as cathode materials for lithium ion batteries were investigated. The specific capacity of LiVO_2 was greatly improved to 149 mAh/g under the current density of 149 mA/g, in comparison with that of the conventional LiVO_2 below 50 mAh/g prepared by the solid-state reactions.

I. Introduction

LAYERED rock-salt type oxides with composition LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$) have attracted much attention as high-energy density cathode materials for lithium rechargeable batteries.^{1–3} Because of the expensiveness of the LiCoO_2 cathode presently used, the synthesis and electrochemical properties of its analogues such as LiNiO_2 ,^{4–8} LiMnO_2 ,^{9,10} $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$,¹¹ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ¹² have been investigated extensively as substitutes for LiCoO_2 . LiNiO_2 shows similar potential curves 0.25 V lower than LiCoO_2 over the entire region, but it is structurally unstable and tends to release oxygen upon electrochemical delithiation.^{4–8} Layered LiMnO_2 transforms to a spinel phase during charge processes and shows poorer cycling stability than the ideal spinel phase LiMn_2O_4 .^{9,10}

LiVO_2 has a layered rock-salt type rhombohedral structure with the space group symmetry $R\bar{3}m$.¹³ While a great number of studies have been reported on the electric, electrochemical, and magnetic properties of the $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$ system crystallizing into three phases, namely LiVO_3 , Li_3VO_4 , and LiV_3O_8 ,^{14–19} there have been a limited number of reports on the electrochemical properties of the layered LiVO_2 .^{20–26} The specific capacity of the layered LiVO_2 has been reported to be ~50 mAh/g due to an irreversible structural change upon delithiation. In the layered LiVO_2 structure, the vanadium and lithium ions occupy the octahedral sites in the cubic close-packed oxygen lattice, forming alternate layers of vanadium 3a (0, 0, 0) and lithium 3b (0, 0, 1/2). The irreversible structural change is due to the rearrangement of the 3a vanadium ions to both the 3a and 3b sites upon delithiation. To suppress the structural instability upon delithiation, an off-stoichiometric $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ ¹⁵ or a solid solution of LiVO_2 and Li_2TiO_3 ¹⁷ have been synthesized in earlier reports. LiVO_2 has been prepared by the

conventional solid-state reaction, heating the mixture of V_2O_5 and Li_2CO_3 in H_2 at 500°C–750°C,^{13,27,28} whereas off-stoichiometric $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ was prepared by a hydrothermal reaction between V_2O_3 and $\text{LiOH}-\text{H}_2\text{O}$ solution at 180°C.

We have developed new routes for synthesizing metal oxides from peroxo-polymetallic acid obtained by direct reaction of metallic powders with hydrogen peroxide solution. Our synthetic methods have advantages in preparation of homogeneous and fine powders, because raw materials are mixed equally at nanometer scale unlike the powder mixtures for the solid-state reactions. They are appropriate for the synthesis of nanosized particles as well as metastable phases forming at low temperatures. For example, peroxo-polytungstic acid is obtained by vigorous reaction between metallic tungsten powder and hydrogen peroxide solution, and an amorphous precursor is precipitated by mixing an alkali solution with the peroxo-polytungstic acid.^{29–32} Heating the precursor at 500°C–700°C yields alkali tungstates or tungsten bronzes.^{33–35} Similarly, molybdenum, niobium, vanadium, titanium, and their carbide powders react with hydrogen peroxide, and yield the corresponding peroxo-polymetallic acids.^{36–39} Synthesis of nanosized perovskite BaTiO_3 and KNbO_3 were achieved by heating the salts of peroxo-polytitanic acid and peroxo-poly niobic acid at 650°C, respectively.^{40,41} A new type of V_2O_5 was also synthesized from peroxo-polyvanadate and its discharge/charge properties as a cathode material for rechargeable lithium batteries were investigated.^{42–45} However, the cathodes for lithium ion batteries must be lithiated materials which act as lithium sources for carbon anodes in charge processes. We aimed at synthesizing nanosized lithium vanadate for cathode materials of lithium ion batteries through a new route. In this article, we describe the synthesis and electrochemical properties of a nanosized-layered LiVO_2 .

II. Experimental Section

(1) Synthesis

Metallic vanadium powder (0.25 g, 100%, smaller than 75 μm , as received from Kojundo Chemical Laboratory, Saitama, Japan) was dissolved in 100 mL of 30 wt% H_2O_2 solution (Wako Pure Chemical Industries, Osaka, Japan) at 20°C with stirring. An orange-yellow transparent solution of peroxo-polyvanadic acid (denoted as V-iPA where iPA stands for isopolyacid) was obtained in 24 h. After removing insolubles by filtration, we mixed the V-iPA solution with 9.8 mL of 0.05 M LiOH aq solution at Li/V molar ratio 1. By drying the mixed solution at 115°C in air for 24 h, we obtained 0.36 g of pale yellow powder of lithium vanadate. By heating this lithium vanadate at 550°C in air for 24 h and subsequently at 800°C in H_2 for 1 h, we obtained black powder of LiVO_2 .

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(2) Characterization and Electrochemical Measurement

The powder XRD patterns were measured with a diffractometer (XD-D1, Shimadzu, Kyoto, Japan) using graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The X-ray profiles were collected between 10° and 120° of 2θ angles with a step interval of 0.02° . The crystalline parameters of the obtained LiVO_2 were refined by the Rietveld method using the RIETAN-FP program.⁴⁶ The morphology was observed by a scanning electron microscope (SEM, JSM-5610, JEOL, Tokyo, Japan) with an accelerating voltage of 10 kV. The thermal behavior was investigated by thermogravimetry (TG) and differential thermal analysis (DTA; DTG-50, Shimadzu, Kyoto, Japan) at a heating rate of $20^\circ\text{C}/\text{min}$ in air.

For charge/discharge measurements, 10.0 mg of LiVO_2 was intimately ground with 10.0 mg of acetylene black (AB, Denki Kagaku Kogyo, Tokyo, Japan), and the composite, after mixing with polytetrafluoroethylene (PTFE) binder, was pressed onto a nickel mesh with area of $1.0\text{ cm} \times 1.0\text{ cm}$. Mesocarbon microbeads (MCMB25-28, Osaka Gas Chemicals, Osaka, Japan) was used as a counter electrode and Li as a reference electrode. A 1 M LiPF_6 EC/DEC solution (EC:DEC=1:1 in volume, Kishida Chemical, Osaka, Japan) was used as an electrolyte. The measurements were carried out in the galvanostatic mode at 1.49 mA (149 mA/g). All materials for electrochemical measurements were stored and handled in an Ar-filled glove box.

III. Results and Discussion

The XRD patterns for the samples heated at 115°C in air for 24 h, at 550°C in air for 24 h and at 800°C in H_2 for 1 h are shown in Fig. 1. The dry residue of the solution at 115°C for 24 h was composed of low crystalline $\text{LiVO}_3 \cdot 0.5\text{H}_2\text{O}$ (PDF-390371) and other unidentified compounds. Subsequent heating at 550°C for 24 h yielded white powder sample whose XRD pattern was coincident with that of the monoclinic LiVO_3 (PDF-251100). By reducing this at 800°C in H_2 for 1 h, we obtained black powder sample whose XRD pattern was coincident with that of the layered LiVO_2 (PDF-360040). The structural parameters of the LiVO_2 from the Rietveld refinement are summarized in Table I. The XRD data were well fitted with the space group $R\bar{3}m$ except for some slight peaks from impurities. This structure is comprised of successive layers of vanadium, oxygen, and lithium ions normal to c axis, where the vanadium and lithium ions have ordered arrangements occupying the $3a(0, 0, 0)$ and $3b(0, 0, 1/2)$ sites, respectively. The crystallite size was estimated at 47 nm using the Scherrer equation, and this is much smaller than the formerly reported results using the conventional solid-state reactions. The SEM image of the LiVO_2 is shown in Fig. 2. The image showed aggregates

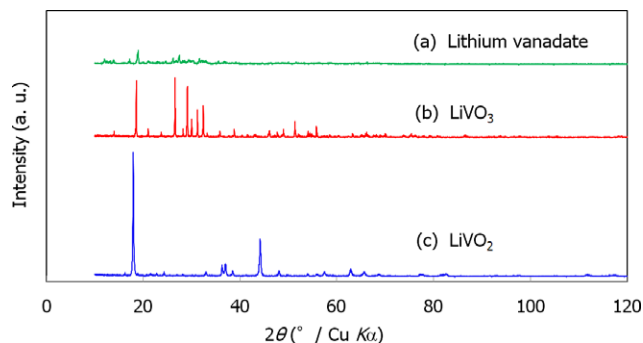


Fig. 1. XRD patterns of (a) lithium vanadate such as $\text{LiVO}_3 \cdot 0.5\text{H}_2\text{O}$ obtained as a dry residue of V-iPA solution at 115°C , (b) LiVO_3 obtained by heating the lithium vanadate at 550°C in air for 24 h, and (c) LiVO_2 obtained by heating the LiVO_3 at 800°C in H_2 for 1 h.

smaller than $10\ \mu\text{m}$ and no grown crystals. The aggregates are considered to consist of secondary particles of the nanosized LiVO_2 . In short, nanosized-layered LiVO_2 was successfully prepared through the new route starting from the reaction between metallic vanadium powder and H_2O_2 aq.

The TG-DTA curves are shown in Fig. 3. LiVO_2 showed a weight increase by 17.9% at 400°C – 700°C in air. This weight increase is due to the oxidation of LiVO_2 and coincident with the theoretical weight increase 17.8% accompanied by oxidation from LiVO_2 to LiVO_3 . In part of the oxidation process at 600°C – 700°C , the DTA curve showed a broad endothermic peak in contrast to an exothermic peak at 400°C – 600°C , and the increasing rate of the TG curve declined correspondingly. This is attributed to melting of the sample. Similar behavior of lithium vanadium oxide has been reported in an earlier study.¹⁵ A small endothermic effect observed at around 212°C is due to the phase transition of LiVO_2 , which has been a hot research topic for its unusual magnetic, electrical, and thermal properties.²⁸ The TG-DTA and XRD results confirmed that the composition formula of the product was LiVO_2 .

Table I. Refined Crystallographic Data for LiVO_2 Obtained by Reducing LiVO_3 in H_2 at 800°C

Hexagonal; space group; $R\bar{3}m$ (166) $Z = 3$				
$a = 0.28471(3)$ nm, $c = 1.4827(1)$ nm				
Atom	Site	Atomic position	Distance (nm)	
Li	$3b(0, 0, 1/2)$		Li–Li	0.2847
V	$3a(0, 0, 0)$		Li–O	0.2113
O	$6c(0, 0, z)$	$z: 0.2562(5)$	V–O	0.2002

All the occupancies were fixed at unity.

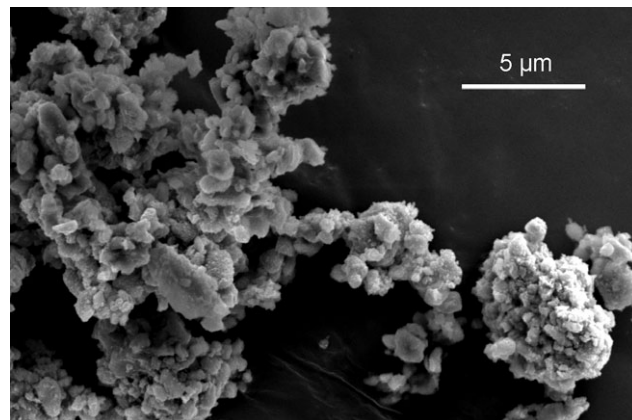


Fig. 2. SEM image of LiVO_2 sample prepared from V-iPA solution.

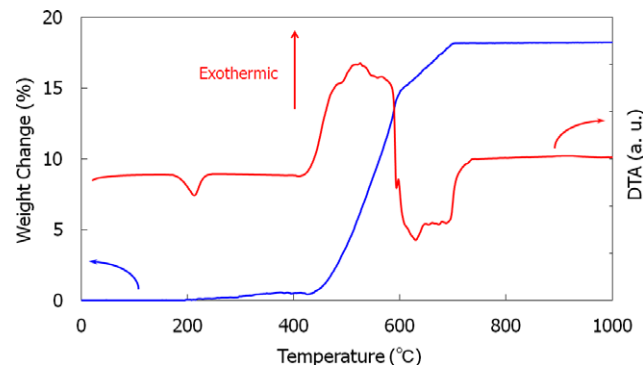


Fig. 3. TG and DTA curves of LiVO_2 sample at a heating rate of $20^\circ\text{C}/\text{min}$ in air.

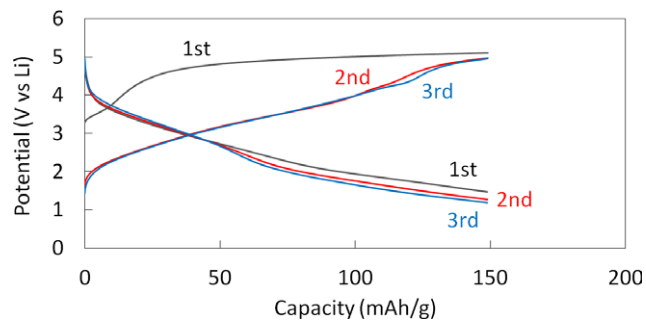


Fig. 4. Charge-discharge curves of LiVO_2 sample at a constant current density of 149 mA/g.

The charge-discharge curves of LiVO_2 at a constant current density of 149 mA/g are shown in Fig. 4. The potential showed a roughly linear increase and decrease without plateaus in the charge and discharge curves, respectively, and the second and third cycles followed almost the same track. The capacity was 149 mAh/g and this indicates the reversible extraction and insertion of lithium ions between LiVO_2 and $\text{Li}_{0.5}\text{VO}_2$. We also investigated the charge-discharge cycles between LiVO_2 and $\text{Li}_{1-x}\text{VO}_2$ for $x = 0.6-1.0$ to determine the composition range over which lithium ions are reversibly extracted and inserted (not shown in figure). For the cycles charging up to $\text{Li}_{1-x}\text{VO}_2$ ($x = 0.6-1.0$), the charge-discharge curves showed deviations from those in the former cycle, and the deviations were increased with increasing x . These results indicate that lithium ions are reversibly extracted from the present LiVO_2 up to $\text{Li}_{0.5}\text{VO}_2$ corresponding to specific capacity 149 mAh/g, whereas the extraction of lithium ions from $\text{Li}_{1-x}\text{VO}_2$ ($x > 0.5$) brings about an irreversible structural change. An earlier study has reported that vanadium disordering, migration from the 3a site to the 3b site, occurred in $\text{Li}_{1-x}\text{VO}_2$ ($x > 0.3$) and inhibited reversible lithium extraction and insertion, which resulted in the low-specific capacities below 50 mAh/g.¹³ Such irreversibility was not observed for the present nanosized LiVO_2 , probably because the reduction in the particle size enhanced the structural stability and suppressed the disordering. We can say that the specific capacity was significantly improved to 149 mAh/g by preparing nanosized LiVO_2 .

IV. Conclusions

Layered rock-salt LiVO_2 with crystallite size 47 nm was successfully prepared through a new route from peroxo-polyvanadic acid. The specific capacity as a cathode of lithium ion batteries was 149 mAh/g under rather high current density of 149 mA/g. The capacity was significantly improved compared with the conventional LiVO_2 obtained by the solid-state reaction (~50 mAh/g), probably because nanocrystallite is structurally stable during lithium insertion and deinsertion.

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