

Short communication

Structural modifications caused by electrochemical lithium extraction for two types of layered LiVO_2 ($R\bar{3}m$)

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Abstract

Two types of layered compounds, $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ ($R\bar{3}m$), were synthesized with a solid-state and a hydrothermal reaction, respectively, and their structural modifications caused by electrochemical lithium extraction were investigated. The $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ compounds are characterized by the ordered and disordered arrangement of vanadium ions in the alternate layers of octahedral 3a (000) and 3b (00 1/2) sites, respectively. According to the electrochemical lithium extraction, the $\text{Li}_{0.96}\text{VO}_2$ changed to a disordered arrangement; such a structural modification is irreversible and takes place in the initial stage of the lithium extraction. For the $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$, no significant structural modification was detected.

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1. Introduction

The layered oxides of LiMO_2 ($M = \text{Co}, \text{Ni}$ or Mo) are of interest as a cathode material for lithium secondary batteries [1–3]. In fact, some of these compounds have already been used in commercial applications. However, LiNiO_2 is structurally unstable as a result of electrochemical lithium extraction or insertion [4], and, thus, wide commercial applications are not possible. In this connection, recent studies have shown that the cationic substitution for nickel in LiNiO_2 is effective for modifying the structural properties [5,6].

LiVO_2 has a structure that is similar to that of LiNiO_2 ; it is characterized as a layered rhombohedral structure related to α - NaFeO_2 , corresponding to the space group symmetry of $R\bar{3}m$ [7,8]. The structure of LiVO_2 takes successive layers of vanadium, oxygen, and lithium ions. The vanadium and lithium ions

occupy the octahedral sites of a cubic close packing of oxygen ions, where the vanadium, lithium, and oxygen ions are positioned at the 3a (000), 3b (00 1/2), and 6c (00*x*) sites, respectively. It was also reported that a similar structural destabilization occurs in the LiVO_2 .

Recently, we synthesized two types of LiVO_2 , namely, $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$, and found that these compounds are characterized by the ordered and disordered arrangements of vanadium ions in alternate layers of octahedral 3a and 3b sites. We also found significant differences in the electrochemical properties of both materials.

In this paper, we discuss the structural modifications due to electrochemical lithium extraction and insertion. Secondly, the electrochemical properties for both materials are reported in connection with their structural modifications.

2. Experimental

The materials of $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ were synthesized through a solid-state and a hydrothermal reaction,

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respectively. In short, for $\text{Li}_{0.96}\text{VO}_2$, equal molar quantities of Li_2CO_3 and V_2O_5 powders were reacted under flowing hydrogen, initially at 500°C for 3 h and then at 700°C for 10 h [7]. For $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$, V_2O_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ for the molar ratio of $\text{LiOH}\cdot\text{H}_2\text{O}/\text{V}_2\text{O}_3 = 20$ were hydrothermally reacted at 180°C for 4 days. After filtration with suction and washing with water, the product was dried at 70°C to give a black powder of $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$.

The lithium and vanadium contents of the resulting materials were determined by inductively coupled plasma (ICP) atomic emission spectrometry. For the structural investigations, powder X-ray diffraction (XRD) experiments were performed using a rotating cathode X-ray diffractometer (JEOL JDX3500) at 35 kV and 300 mA with a 2θ - θ step-scanning mode and graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Rietveld refinements based on the XRD data were also conducted using the RIETAN computational program system [9].

Electrochemical lithium extraction and insertion were conducted using a coin-type cell with Li metal as an anode and a 1 mol dm^{-3} LiClO_4 solution in mixed ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) as an electrolyte. The cathodes consisted of a titanium grid on which the dried materials (ca. 14 mg), mixed with 20 wt% carbon black and 10 wt% polytetrafluoroethylene (PTFE) powders, were pressed. The electrochemical lithium extraction and insertion were performed at current densities of $\pm 7.14 \text{ mA g}^{-1}$ in the cell voltage range of 1.5–4.5 V.

3. Results and discussion

The results of chemical analyses by ICP are summarized in Table 1. The measurements of thermogravimetry (TG), not shown here, indicate that adsorbed or structural water rarely exists in the resulting materials. Thus, the compositions can be represented to be $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$, respectively, for materials prepared by the solid-state and hydrothermal reactions.

Fig. 1 shows the XRD profiles of the resulting materials of $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$. Each profile shows differences, especially regarding the significantly reduced intensity of the 003 reflection at $2\theta \sim 18^\circ$ for the material of $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ [7]. By simulation, using model structures, it was confirmed that this behavior primarily takes place according to the disordered arrangement of vanadium ions into 3b sites. Fig. 2 shows the simulated XRD profiles of the LiVO_2 materials with various levels of such disordered arrangement, which were calculated using a computational program system (CaRIne crystallography). We found that the intensity of the 003 reflection decreases with an

Table 1

Results of chemical analyses by ICP for the compounds synthesized by the solid-state reaction (a) and hydrothermal reaction (b)

	Compound	
	Li content (wt%)	V content (wt%)
a	7.44	56.8
b	7.57	51.7

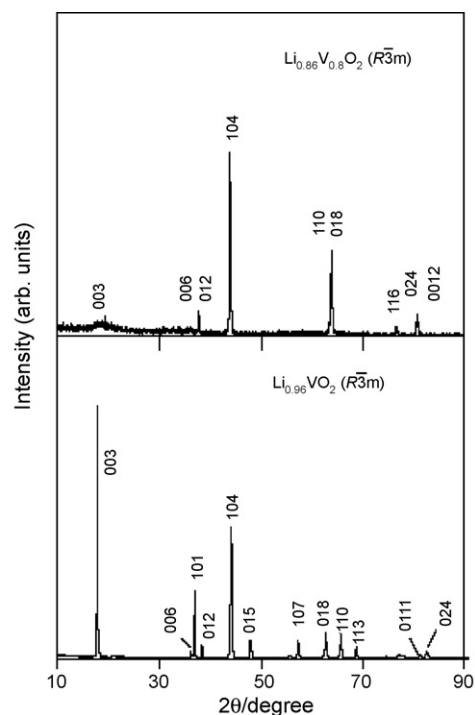


Fig. 1. XRD profiles of the materials of $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$.

increase in the vanadium occupancy for the 3b site and is nearly zero for the value of 0.55 (Fig. 2(a)). The 003 reflection is due to the layered rock-salt structure of Rm , whereas the 104 reflection results from the layered and cubic rock-salt structures.

Referring to Fig. 1, the profile of $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ shows an extraordinary reduced intensity of the 003 reflection compared to that of $\text{Li}_{0.96}\text{VO}_2$. This fact suggests that the structure of

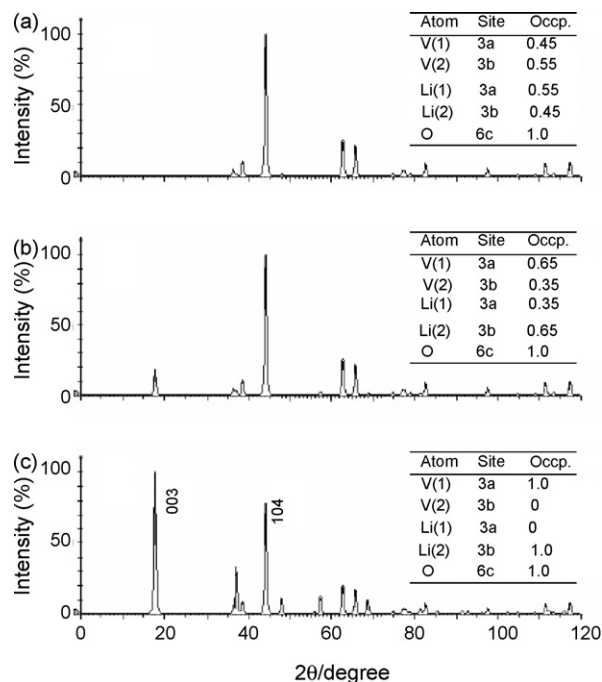


Fig. 2. Simulated XRD profiles for LiVO_2 materials with various levels of a disordered arrangement of vanadium ions at the 3a and 3b sites.

Table 2
Summary of the refined structural parameters of the $\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$

Lattice parameter (Å)	Atom	Position	Occupancy	B value (Å ²)	R factor
$a = 2.9100(5)$, $b = 14.230(2)$ ($R\bar{3}m$)	V(1)	3a (000)	0.358(5)	0.7(2)	$R_{\text{wp}} = 0.144$ $R_{\text{exp}} = 0.070$ $R_{\text{F}} = 0.115$
	V(2)	3b (00 1/2)	0.442(5)	0.6(2)	
	Li(1)	3a	0.56	0.7(2)	
	Li(2)	3b	0.30	0.6(2)	
	O	6c (00 x), $x = 0.2464(6)$	1.0	1.0	

$\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$ is comprised of the disordered arrangement of vanadium ions at the 3a and 3b sites. In fact, for the material of $\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$, we found that the Rietveld refinement based on the XRD data only converges for the disordered arrangement of the vanadium ions. The refined parameters for the Rietveld refinement are summarized in Table 2. Here, it is noted that the precise crystallographic information on lithium ions cannot be determined based on the XRD data alone; thus, we are conducting the Rietveld refinement on the basis of the neutron diffraction data.

To clarify the structural modifications caused by electrochemical lithium extraction for the materials, the XRD profiles of the materials at various stages of electrochemical lithium extraction and insertion are shown in Figs. 3 and 4. It is noteworthy that the XRD measurements were conducted using the cathode samples with a titanium grid, and, thus, reflections due to titanium are observed in almost every profile. For $\text{Li}_{0.96}\text{VO}_2$ (Fig. 3), except for the initial sample, a sig-

nificantly reduced 003 reflection is observed in each profile, which indicates that vanadium disordering takes place at least when $x \leq 0.74$ for the composition of Li_xVO_2 . In addition, since the profile of $\text{Li}_{0.65}\text{VO}_2$ (Fig. 3(d)), which was obtained through the electrochemical insertion process followed by the lithium extraction process, also shows a reduced 003 reflection, such vanadium disordering is an irreversible modification. On the other hand, for $\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$ (Fig. 4), no apparent structural modification was detected, indicating structural stability.

It appears that such structural properties of $\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$ influence their electrochemical performance. Fig. 5 shows the variation in the cell voltage versus the amount of lithium for the $\text{Li}/\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}/\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$ cells according to the lithium extraction and insertion. A significant hysteresis was detected for the $\text{Li}/\text{Li}_{0.96}\text{VO}_2$ cell, whereas almost symmetrical behavior was observed for the $\text{Li}/\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$ cell. These events could be primarily responsible for their structural behavior. Here, it is noteworthy that not every electrochemical performance can be explained by such structural modifications. In particular, the electrochemical capacities of the materials could be related to the presence of vanadium vacancies. In connection with this, a quantitative study using neutron measurements is underway.

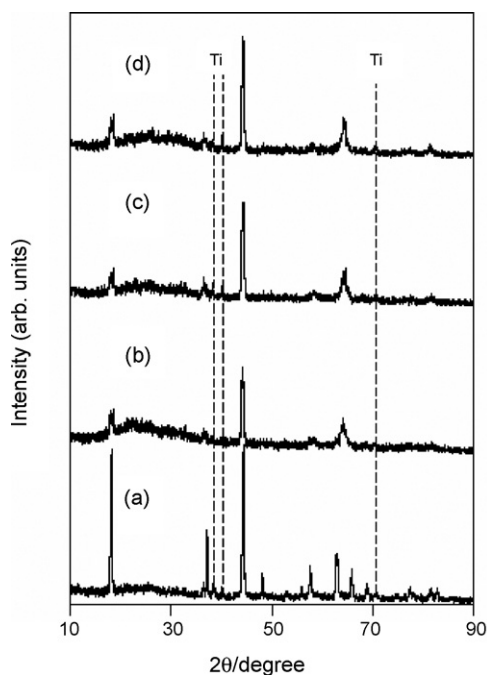


Fig. 3. XRD profiles of the cathode samples for the $\text{Li}_{0.96}\text{VO}_2$ materials at various stages of electrochemical lithium extraction or insertion: (a) the initial sample ($\text{Li}_{0.96}\text{VO}_2$); (b) and (c) the samples obtained by the lithium extraction process, corresponding to the compositions of $\text{Li}_{0.74}\text{VO}_2$ and $\text{Li}_{0.64}\text{VO}_2$, respectively; (d) the sample obtained by the lithium insertion process followed by the lithium extraction process, corresponding to the composition of $\text{Li}_{0.65}\text{VO}_2$.

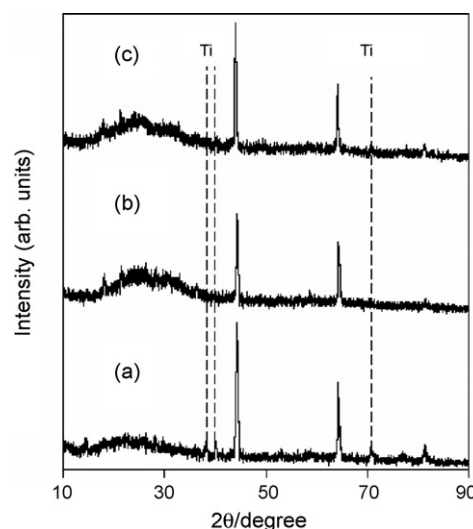


Fig. 4. XRD profiles of the cathode samples for the $\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$ materials after the electrochemical lithium extraction and insertion processes: (a) the initial sample ($\text{Li}_{0.86}\text{V}_{0.8}\text{VO}_2$), (b) the sample after the first lithium extraction process ($\text{Li}_{0.52}\text{V}_{0.8}\text{VO}_2$) and (c) the sample after the lithium insertion process ($\text{Li}_{0.87}\text{V}_{0.8}\text{VO}_2$).

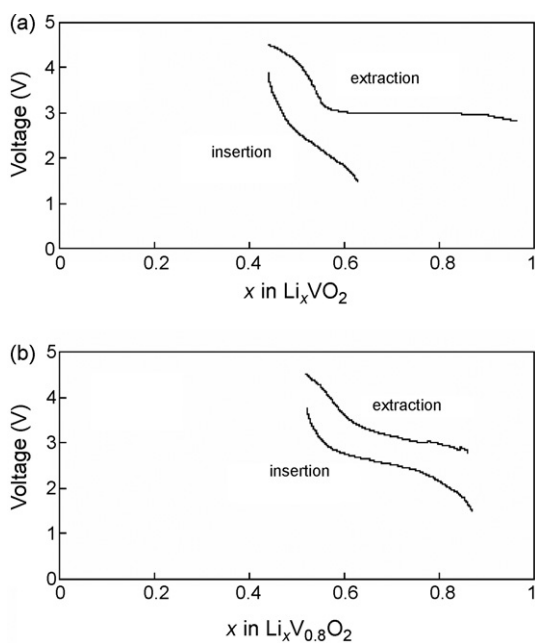


Fig. 5. Variation of the cell voltage vs. the amount of lithium according to the electrochemical lithium extraction and insertion processes for the $\text{Li}/\text{Li}_{0.96}\text{VO}_2$ (a) and $\text{Li}/\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$ (b) cells, covering the cell voltage of 1.5–4.5 V.

4. Conclusions

We have demonstrated the preparation of two types of layered compounds ($\text{Li}_{0.96}\text{VO}_2$ and $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$) and their structural modifications according to electrochemical lithium extraction or

insertion. The material of $\text{Li}_{0.96}\text{VO}_2$ is transformed into the disordered structure of vanadium ions at the 3a and 3b sites, and this transformation is an irreversible change and occurs at the initial stage of lithium extraction. On the other hand, no apparent structural modification was observed for the material of $\text{Li}_{0.86}\text{V}_{0.8}\text{O}_2$. The results also show that such structural properties influence their electrochemical performance.

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