Structural Changes of Vanadium Pentoxide Xerogel by the Electrochemical Lithiation in a Propylene Carbonate Solution

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The structural changes of vanadium pentoxide xerogel ($V_2O_5 \cdot nH_2O$) caused by the electrochemical lithiation in a 1 mol dm^{-3} $LiClO_4$ -propylene carbonate (PC) solution have been investigated. The interlamellar distance decreases slightly with $x = (Li/V)$, though it increases when immersed in PC or an electrolyte solution without the cathodic reduction. IR absorption spectra showed that the chemical bond between hydrogen of interlamellar water and oxygen in a $V=O$ site is broken at the initial stage ($x < 0.2$) and that layered V_2O_5 ribbon unit is also destroyed gradually with increasing x . The intercalation of propylene carbonate was confirmed by the IR spectroscopy.

1. INTRODUCTION

As mentioned previously [1-3], vanadium pentoxide xerogel (VXG, $V_2O_5 \cdot nH_2O$) one of water-containing transition metal oxides, can be expected as a candidate for the positive pole material in a lithium battery. So far, the lithiation of VXG was investigated both electrochemically [1, 4] and chemically [2, 3], where the electrochemical processes were also studied for the electrochromic application [5]. In this work, the structural changes of VXG caused by the electrochemical lithium insertion in a propylene carbonate (PC) solution have been investigated mainly by IR absorption and X-ray diffraction analyses and compared with those observed on the chemical lithiation by LiI [3].

2. EXPERIMENTAL

2.1 Preparation and characterization of vanadium pentoxide xerogel

A thin film (thickness *ca.* $7 \mu\text{m}$, area *ca.* 1.5 cm^2) of VXG having an n -value of 2.2 was prepared [2] on a microscopic cover glass with an evaporated nickel (or gold) layer. The amount (*ca.* 2.5 mg) of VXG was determined by the weight gain of the substrate on a digital (10^{-5} g digit) balance.

X-ray diffraction from a VXG film was measured in the reflection geometry using $CuK\alpha$ radiation at $3 \text{ deg} < 2\theta$ (lattice spacing $< 2.95 \text{ nm}$) with a scanning rate of $0.25 \text{ deg}(2\theta) \text{ min}^{-1}$. The interlamellar distance, d_{001} , was calculated

as an average value from the diffraction angle of $(00l)$ ($l = 1, 3, 4$ and 5) harmonics. IR absorption spectra from 500 to 3800 cm^{-1} were obtained by a Perkin-Elmer 983G instrument using KBr disks.

2.2 Electrochemical lithiation

As in a previous study [1], the lithiation was carried out galvanostatically at 25°C in a 1 mol dm^{-3} $LiClO_4$ -PC solution where the potential was referred to a reversible lithium electrode in the electrolyte. To avoid the reduction of PC, the applied current was terminated when the potential went down to 2.0 V . If necessary, the successive lithiation was started after waiting the potential recuperation.

An extent of the lithiation, $x = (Li/V)$ atomic ratio, was calculated from the amount of passed charge by assuming that one Li^+ ion is inserted per one electron. A lithiated sample was washed with pure acetonitrile more than three times then dried in a silica gel desiccator at room temperature before the analysis.

3. RESULTS AND DISCUSSION

3.1 The electrochemical aspects

The open-circuit potentials of nine virgin electrodes were in a range of $3.85 \sim 3.20 \text{ V}$ (3.55 V in average) after 1200 min immersion. These wide-spread spontaneous potentials may suggest the lack of reversible potential determining reaction at the unlithiated VXG-electrolyte interface.

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The galvanostatic reduction potential, on the other hand, was reproducible to some extent as seen in Fig. 1. The potential plateau at around 2.9 V will be high enough for a positive pole material when -0.2 A m^{-2} was applied per geometrical area. If we suppose that these curves were quasi-equilibrium, the sharp potential descendance at around $x = 0.3 \sim 0.4$ corresponds to the first thermodynamical limit of lithiation. This is recognized more clearly on the succeeding intermittent discharge curves, where little residual capacity is observed.

Fig. 1 Galvanostatic discharging curves
current density; -0.2 A m^{-2}

* for ** and a rough scale for other electrodes within an error of $\pm 8\%$

The final recuperation potential, at which its time derivative diminishes below 2 mV h^{-1} , was plotted in Fig. 2 against x . Curve 1 in this figure is our previous coulometric titration data [1] obtained by using a thicker VXG plate (*ca.* 0.1 mm) and far smaller discharge steps ($\Delta x \approx 0.02$) than in this work. Curve 2 in this figure, on the other hand, shows the open-circuit immersion potential of lithiated VXG by a reducing agent of LiI [2]. The potential of these samples should be identical, if the same product was obtained independent of lithiation procedures and if the potential was determined by the following cell reaction.

The first assumption is invalid, however, since an electrochemically lithiated sample contains PC molecules as shown below though no solvent (acetonitrile, AN for LiI) molecule is detected in chemically lithiated one. We suspect that inserted PC molecules affect the state of Li^+ ions to lower the potential by *ca.* 0.2 V and that plotted data (○) are virtually on the precise coulometric titration curve (curve 1).

Fig. 2 Changes in the open-circuit potential with an extent of the lithiation

1; electrochemical lithiation, ref.[1]

○; this work

2; chemical lithiation, ref.[2]

3.2 Change in the interlamellar distance

The X-ray diffraction patterns of lithiated and unlithiated VXGs were shown in Fig. 3. All observed diffraction peaks can be assigned as (00*l*) harmonics, which shows that the orientation of VXG lamellar planes parallel to the substrate is maintained during the lithiation.

The interlamellar distance, d_{001} , was shown in Fig. 4 as a function of x . According to our experimental results (○), d_{001} decreases slightly at the initial lithiation stage ($x < 0.2$), though its drastic increase was reported (●) in the same region of x . After immersed in pure PC and in a

Fig. 3 X-ray diffraction patterns of lithiated VXG films

1; $x = 0$ (as prepared) 2; $x = 0.051$
3; $x = 0.17$ 4; $x = 0.30$

Fig. 4 Change in the interlamellar distance with an extent of the lithiation

○; electrochemical lithiation, this work
●; electrochemical lithiation, ref.[4]
△; chemical lithiation, ref.[3]

$\text{LiClO}_4\text{-PC}$ solution for 6 days, d_{001} increases from its original value of 1.16 nm to 2.13 and 1.67 nm, respectively. The latter value in the electrolyte is considered to correspond to the intermediate intercalation of PC (1.75 nm) [6].

At $0.2 < x$, observed d_{001} tends to remain constant at around 1.05 nm in consistent with the literature data (●) and also with the previous data for chemically lithiated VXGs (△). The above results suggest that the insertion of PC molecules occurs spontaneously and that PC in a VXG host is either expelled or re-oriented by the electrochemical lithiation to decrease an interlamellar gap. The latter possibility is supported by IR absorption data as described below.

3.3 Change in IR spectra

Fig. 5 IR absorption spectra (KBr disk)

1; $x = 0$ (as prepared) 2; $x = 0.089$
3; $x = 0.17$ 4; $x = 0.30$
a; $\nu(\text{O-V})$ b; $\nu(\text{V-O})$
c; $\nu(\text{V=O})$ c'; $\nu(\text{V=O}\cdots\text{H})$
d; PC e; $\delta(\text{H-O-H})$
f; PC

The IR spectra of lithiated and unlithiated VXGs were compared in Fig. 5 for which band assignments were described previously [1, 3]. An additional absorption (f) in a lithiated sample at 1785 cm^{-1} (in a case of curve 3) is attributed undoubtedly to the strongest C=O absorption band of PC [7]. Also several bands at around 1100 cm^{-1} (d) are located close to the absorption peaks of PC.

The relative integrated absorbance of these bands was shown in Fig. 6, where the 580 cm^{-1} band ($\nu(\text{O}-\text{V}, 202 \text{ pm})$) [8] was chosen as a reference arbitrarily. The stronger absorption of PC is observed in the more highly lithiated sample (d). The absorption at 920 cm^{-1} , which is an indicator for the interaction between interlamellar water and the V_2O_5 network, disappears at $0.2 < x$ (c). Although Abello *et al.* [9] pointed out the reaction of VXG with KBr, Fig. 6 shows that $\text{V}=\text{O}$ (b) or $\text{V}-\text{O}$ (a) bond is broken markedly compared with a longer O-V bond.

Fig. 6 Integrated IR absorption intensities relative to the $\nu(\text{O}-\text{V})$ band

(a); $\nu(\text{V}-\text{O}, 178 \text{ pm})$ (b); $\nu(\text{V}=\text{O}, 159 \text{ pm})$
(c); $\nu(\text{V}=\text{O} \cdots \text{H})$ (d); PC ($\sim 1790 \text{ cm}^{-1}$)

4. CONCLUSION

When VXG is lithiated electrochemically in a propylene carbonate solution, the interlamellar distance decreases slightly at the initial stage ($x < 0.2$) whereas the insertion of PC occurs spontaneously without the reduction current. The strong interaction between interlamellar water and layered V_2O_5 ribbon unit disappears at $0.2 < x$, and the oxide unit itself is also destroyed gradually with increasing x . The presence of propylene carbonate molecule in lithiated VXG was confirmed.

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