The Chemical Lithiation of Vanadium Pentoxide Xerogel by LiI in Acetonitrile Solutions

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The chemical lithiation of vanadium pentoxide xerogel ($V_2O_5 \cdot 2.2H_2O$) was investigated using LiI-acetonitrile solutions. In the first stage of this reaction, an extent of the lithiation x defined as (Li/V) atomic ratio in the xerogel phase tends to saturate at around 0.28 against the concentration of a reducing agent, LiI. On the electrode potential vs. x curve, an inflection point appears also at $x=0.28$.

1. INTRODUCTION

The electrochemical insertion of lithium into vanadium pentoxide xerogel (VXG), $V_2O_5 \cdot nH_2O$ of which structure and properties had been revealed almost thoroughly by Livage and co-workers (1-2), was investigated in a $LiClO_4$ -propylene carbonate solution by themselves (3). From X-ray diffraction studies, they concluded that two compounds in the Li-V-O ternary system containing no water molecules are formed by the electrochemical lithiation. In a previous work (4), on the other hand, we have studied the electrochemical lithiation of VXG by the galvanostatic intermittent titration technique and reported changes in the open-circuit potential and in the chemical diffusion coefficient of lithium with an extent of the lithiation up to (Li/V) = *ca.* 1.1.

In this work, VXG has been lithiated chemically by a reducing agent of lithium iodide (LiI) in acetonitrile solutions and the change in open-circuit potentials with an extent of the lithiation has been compared with that of electrochemically lithiated VXG.

2. EXPERIMENTAL

2.1 Vanadium pentoxide xerogel

As in a previous study (4), viscous dark red V_2O_5 gel was spread on a glass substrate then dehydrated at 60 °C under atmosphere to obtain

xerogel.

The combined DTA-DTG analysis of powdered VXG showed that the n -value in a formula of $V_2O_5 \cdot nH_2O$ is 2.19 ± 0.05 . In a X-ray diffraction pattern of well-oriented thin film VXG on a glass substrate, only (00 l) harmonics from $l=1$ to $l=5$ were observed. The interlamellar spacing of VXG calculated from the diffraction angle of a (001) line was 1.18 ± 0.08 nm. This is almost the same as a literature (3) value, 1.155 ± 0.005 nm, for $V_2O_5 \cdot 1.6H_2O$.

2.2 Chemical lithiation reaction

About 300 mg of weighed VXG powder (grain size *ca.* 0.1 mm) was put into a 50 cm³ portion of a lithium iodide (LiI)-acetonitrile (AN) solution (5) of which initial concentration was varied from 0.005 to 1 mol dm⁻³. The chemical lithiation was allowed to proceed in a closed glass flask at room temperature until the equilibrium was reached (at least for 2 days). Then an aliquot of solution was titrated by a standardized 0.1 mol dm⁻³ $Na_2S_2O_3$ aqueous solution to determine the reaction product of I_2 . All chemicals used were extra-pure or reagent grade.

An extent of the lithiation, x defined as the atomic ratio of (Li/V), was calculated from the initial weight of VXG and the amount of

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formed I_2 by assuming the following reaction

similarly to the case of crystalline V_2O_5 (5). Though the lithium concentration in VXG was not confirmed by any analytical method in this work, the color of VXG powder changed from brown red to blue black after the lithiation. IR absorption, X-ray diffraction and DTA-DTG results of lithiated VXG will be reported in a succeeding paper (6). Lithiated VXG powder was washed with pure AN then dried at room temperature.

2.3 Open-circuit potential measurements

Sample electrodes were prepared by pressing a mixture of lithiated VXG (80 wt%) and graphite (20 wt%) at a pressure of 200 MPa (2 ton cm^{-2}). The electrochemical cell,

was constructed in a closed glass vessel filled with argon. The open-circuit potential, U_{oc} , was measured with an electrometer (input impedance $> 10^{12} \text{ ohm}$) and a digital (1 mV digit) voltmeter in a thermostat at 25 °C.

3. RESULTS AND DISCUSSION

3.1 Changes in open-circuit potentials with the lithiation

In Fig. 1, the change in U_{oc} of chemically lithiated VXG with x (curve 1) is compared with that of electrochemically lithiated VXG (curve 2, ref.(4)). The partial molar free energy of lithium in the VXG phase at 298 K, μ_{Li} given by $(-F U_{oc})$, is shown on the right-hand side ordinate of this figure, where F denotes the Faraday's constant. In a case of chemically lithiated VXGs, U_{oc} has an inflection point at around $x=0.28$ as seen on curve 1. The coulometric titration curve of VXG in a 1 mol dm^{-3} LiClO_4 -propylene carbonate solution (curve 2), on the other hand, has two inflection points at $x=0.53$ and 0.87 (both beyond this scope) as reported previously (4).

In general, the discrepancy of U_{oc} between chemically and electrochemically lithiated VXGs, which does not exceed 0.4 V at any

Fig. 1 Changes in open-circuit potential with an extent of the lithiation, 25 °C

- 1: VXG, chemical lithiation
- 2: VXG, electrochemical lithiation
- 3: crystalline V_2O_5 , ref.(5)

point of x , may be caused by the difference in electrolyte solutions used for potential measurements and/or the difference in reduction methods (especially kinds of a solvent) employed for lithium insertion. Since organic solvents such as propylene carbonate, dimethylsulfoxide, tetrahydrofuran and so on are intercalated into VXG (3,7), the effect of solvents can appear during both the lithiation and the potential measurement. IR-absorption and DTA-DTG data on chemically lithiated VXG showed that interlamellar water is neither expelled nor replaced by AN (6). At the present time, we suspect that propylene carbonate molecules detected in an electrochemically lithiated sample (4) may affect the state of inserted Li^+ ion.

A sharp increase in μ_{Li} at $x=0.28$ on curve 1 shows that there is a kind of thermodynamical limit for the chemical lithiation at this composition similar to those observed for solid solution electrodes (8). In the case of crystalline V_2O_5 (1), μ_{Li} varies discontinuously at $x=0.25$ and 0.50 as compared in Fig. 1 (curve 3). If we may

approximate the limiting composition of $x = 0.28$ for VXG as $x = 0.25$, then this limit can be attributed to the characteristics of the V_2O_5 unit in VXG as a host for lithium, because V_2O_5 ribbon units are conserved in the VXG structure (9-10).

The Gibbs free energy change at 298 K for the following lithiation reaction

ΔG_3 , which can be obtained by the graphical integration of μ_{Li} with x from $x = 0$ to $x = x$, is shown in Fig. 2 as a function of x (curve 1) comparing with that for crystalline V_2O_5 (curve 2). From these curves, it is clear that the presence of water in VXG does not affect markedly on the free energy change for the lithiation. In other words, the major part of the free energy change may be involved not in the coordination of Li^+ ion in the host matrix but in the reduction of +5 valent vanadium to +4 state.

Fig. 2 The Gibbs free energy change for the lithiation reaction as a function of an extent of the lithiation

1: $V_2O_5 \cdot nH_2O$ ($n=2.19 \pm 0.05$)

2: crystalline V_2O_5 , ref.(5)

3.2 Chemical equilibrium for the lithiation reaction

The lithium concentration x in lithiated VXG was shown in Fig. 3 as functions of final and initial concentrations of LiI in a solution. As can be seen in this figure, the reaction [1] proceeds in two steps, namely $0 < x < 0.28$ and $0.28 < x$. This means that there is the first limit of chemical lithiation at $x = 0.28$ which may be of a thermodynamical nature, because the reaction was allowed to equilibrate.

Fig. 3 Dependence of the lithium content x in VXG on final and initial concentrations of LiI

1: final concentration vs. x

2: initial concentration vs. x

If we suppose that the rate of reaction [1] is controlled by the chemical diffusion of lithium in the VXG phase, a characteristic reaction time will be represented by a time constant of diffusion given by (r^2/D) where r and D are radius of VXG powder and the chemical diffusion coefficient of lithium in VXG, respectively. Since $D = (1 \times 10^{-13} \sim 3 \times 10^{-14} \text{ m}^2 \text{ s}^{-1})$ at $0 < x < 0.4$ (4) and $r = ca. 0.05 \text{ mm}$, this time constant is in the range of $3 \times 10^4 \sim 1 \times 10^6 \text{ s}$ of which maximum value still remains in the order of reaction period longer than 48 h ($1.73 \times 10^5 \text{ s}$). Further, this first lithiation limit at $x = 0.28$ corresponds to the composition at which μ_{Li} increases abruptly as mentioned in 3.1.

The equilibrium constant of the heterogeneous reaction [1], K_1 , was calculated for the first lithiation stage, where final molar concentration was used for LiI and I_2 and the activity ratio of lithiated to unlithiated VXG was replaced by the term of $[x/(0.28-x)]$ according to the Armand's occupied-unoccupied sites treatment of a solid solution electrode (8). The obtained value of K_1 for each initial concentration of LiI was constant at $10-20 \text{ (mol dm}^{-3}\text{)}^{-1/2}$.

4. CONCLUSION

In the lithiation of vanadium pentoxide xerogel ($V_2O_5 \cdot 2.2H_2O$), there is the first thermodynamical limit at around $(Li/V)=0.28$ which, after approximating as $x = 0.25$, is suspected to be a definite composition determined by the characteristics of V_2O_5 units in xerogel.

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