

Characterization of sputtered vanadium oxide films for lithium batteries

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Abstract

Orthorhombic V_2O_5 crystal thin films have been prepared by radio frequency sputter deposition in an argon atmosphere containing 20% oxygen and a V_2O_5 target. The film can undergo reversible charge–discharge cycling. The mass change that takes place during charge–discharge cycling is in good agreement with the lithium value from measurement of the resonance frequency changes of a quartz crystal microbalance. However, during the first few cycles, the amount of mass change differs a little from the lithium value, which may be caused by creation of a surface film on V_2O_5 . During subsequent cycling, the electrode mass continues to increase which that means some part of the inserted lithium can not be extracted. This mass accumulation is clearly related to the origins of the reduced charging capacity of the V_2O_5 films for cathode material of lithium batteries. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Vanadium oxide, known to have a high capacity for lithium insertion [1], is a promising material for rechargeable lithium batteries and especially for polymer batteries. One prospective application of lithium polymer batteries is as on-chip power sources. Such batteries may be made with conventional thin film techniques, such as vapor deposition, electron-beam evaporation, laser ablation and sputter deposition onto integrated circuit industrial quality components.

Recently, stoichiometric V_2O_5 [2,3] has been prepared by radio frequency (rf) sputtering of a V_2O_5 target, and a variety of VO_x compounds [4] have been formed by rf reactive sputtering of a vanadium target in flowing oxygen. These films have been characterized and investigated with regard to their capacities for lithium insertion in lithium secondary batteries.

The electrochemical quartz crystal microbalance (EQCM) method is an in situ mass-sensitive detector based on measurement of the resonant frequency change induced by mass or viscosity changes of a film attached to a quartz crystal substrate during electrochemical measurements. The EQCM method can be used to analyze accompanying

electrode processes, such as electrode position, film growth, ion uptake into polymer films, ionic adsorption and electrochemical intercalation, and has been used to investigate the surface films on lithium metal anodes caused by reaction with the adjoining electrolyte of lithium batteries [5–7].

In the studies described herein, we prepared vanadium oxide thin films by rf sputtering and investigated their electrochemical performance for lithium batteries via galvanostatic charge–discharge measurements and analyzed lithium insertion and extraction processes using EQCM measurements. We have also attempted to identify the chemical constituents inserted into (extracted from) oxide films during charge–discharge cycling.

2. Experimental

The deposition of the vanadium oxide films used in this study was accomplished with a 13.56-MHz rf reactive sputtering apparatus, i.e., the ULVAC model MUE-201C-HC3. The V_2O_5 target consisted of pressed and sintered 99.99% V_2O_5 powder (Rare Metallic). The V_2O_5 was deposited on SiO_2 or on a nickel film coated with a quartz crystal substrate in an atmosphere of argon gas containing 20% oxygen. The rf power was 150 W. The thickness of the deposited films was typically about 250 nm.

Characterization of the deposited films was accomplished with scanning electron microscopy (SEM) and

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with X-ray diffraction (XRD) using $\text{CuK}\alpha$ irradiation. The electrochemical and EQCM experiments were performed in three-electrode beaker type cells using a Biologic Science Instruments model Mac Pile II charge/discharge experimental unit and a Hokuto Denko model HQ-101B QCM control unit with a model HQ-201 QCM oscillator unit interfaced with a NEC PC 9801 personal computer. A 6 MHz AT-cut quartz crystal with a 1.5-cm^2 active area of nickel was used as the substrate for electrochemical and EQCM measurements. The reference and counter electrodes were lithium metal (battery grade, Honjo Metal). The electrolyte used was a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing a 1.0 mol dm^{-3} LiClO_4 solution (battery grade, Tomiyama Pure Chemical Industries). The solutions initially contained less than 20 ppm of H_2O measured using the Karl Fischer moisture meter and every electrochemical measurement was made in an argon atmosphere.

3. Results and discussion

Fig. 1 shows typical XRD patterns of a sputtered vanadium oxide film on a SiO_2 substrate (Fig. 1a) and V_2O_5 target (Fig. 1b). Although the XRD pattern had a much lower intensity, it could be assigned as orthorhombic V_2O_5 as the result of sputtering. Fig. 2 shows the SEM image of typical as-prepared vanadium oxide films on a quartz crystal. The surface of the vanadium oxide film is almost flat and each crystallite is tightly interconnected. All the particles of vanadium oxide in this film can act as an electrode material without binder.

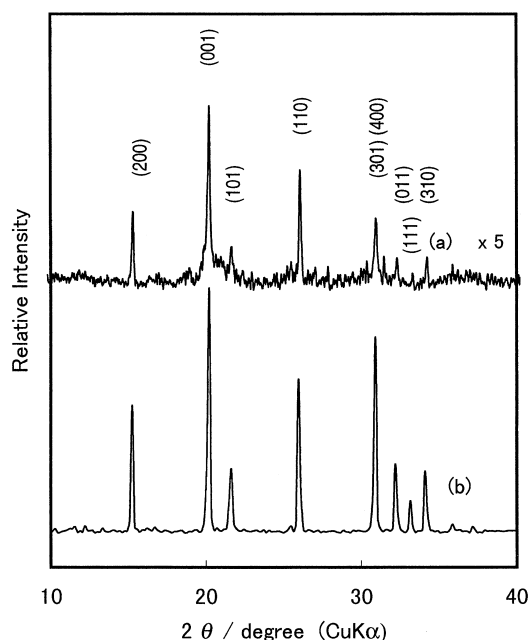


Fig. 1. XRD pattern of vanadium oxide film (a) and V_2O_5 target (b).

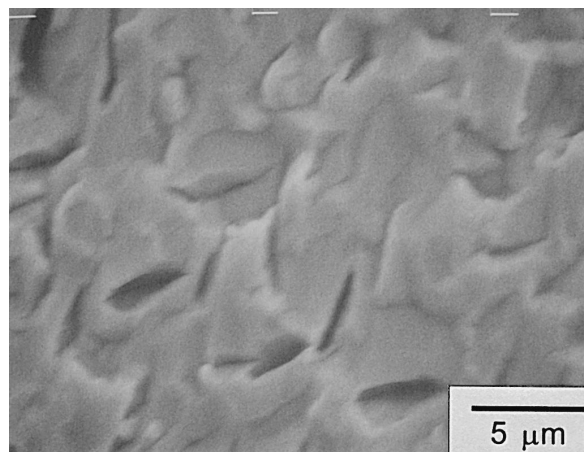


Fig. 2. SEM image of sputtered vanadium oxide film.

The galvanostatic charge–discharge cycling curves of a sputtered vanadium oxide film are shown in Fig. 3. The first cycle shows a stepwise discharge curve with three plateaus at 3.35 V, 3.18 V and 2.30 V. The curve shape at the first cycle is same to that of crystalline V_2O_5 with the three plateaus corresponding to $\alpha + \epsilon$, $\epsilon + \delta$ and $\delta + \gamma$ phase mixtures, respectively [8]. The discharge curves following cycle, these plateaus disappear with repeated cycling. This behavior is irreversible phase transformation and the charge–discharge profile finally approaches that of a typical amorphous V_2O_5 curve. Fig. 4 shows the changes recorded in the quartz resonance frequency (Δf) during the galvanostatic charge–discharge measurements. The Δf decreases continuously during discharge, which signifies an increase in the electrode mass, corresponding to lithium insertion into the vanadium oxide. During charging, the Δf continuously increases, which corresponds to a decrease in

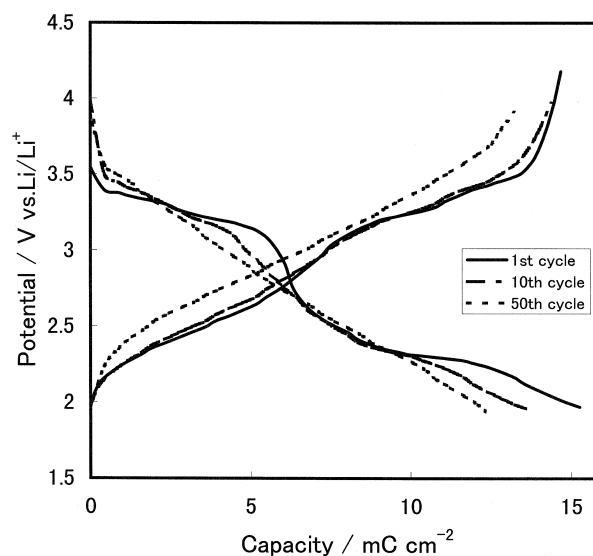


Fig. 3. Galvanostatic charge–discharge cycle curves of vanadium oxide film; current density: 0.04 mA cm^{-2} , discharge cut off voltage: 2.0 V, discharge cut off voltage: 4.0 V.

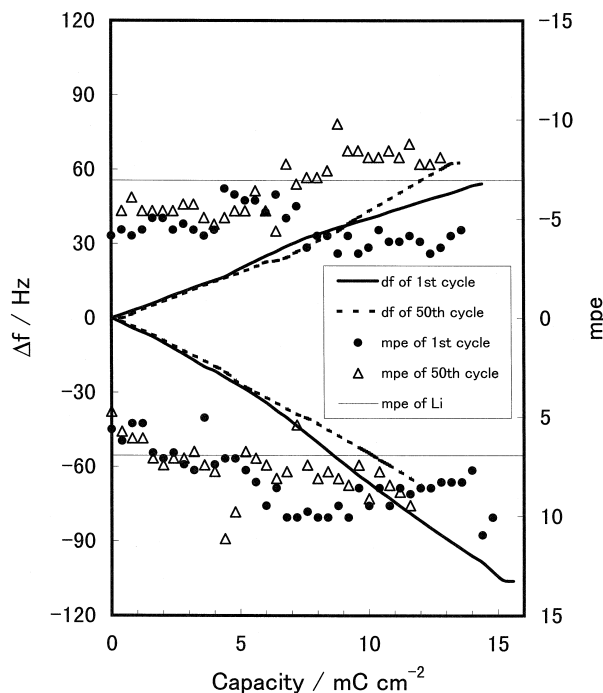


Fig. 4. Quartz resonance frequency change (Δf) during the galvanostatic charge-discharge cycles (Fig. 3) and equivalent weight of the inserted (or extracted) species calculated from Δf .

the electrode mass and lithium extraction from the vanadium oxide. The Δf profiles did not show any significant difference, other than inclination, between the crystalline-like first cycle and the amorphous-like 50th cycle. Fig. 4 also shows a more direct example using the equivalent weight of the inserted (or extracted) species compared to the mass accumulated per mole of electrons transferred (mpe) calculated via the resonance frequency shift of the EQCM using the Sauerbrey relationship [9].

$$\text{mpe} = \frac{d\Delta m}{dQ} F = \frac{d\Delta f}{dQ} \frac{F}{C_f}$$

Where Δm and Q is mass accumulation and charge per unit area, respectively. F is the faraday number and C_f is the correlation coefficient between Δm and Δf . At the low voltage plateau region of the first discharge (Fig. 3), the experimental mpe of the inserted species is heavier than the mpe of lithium (6.9). Solvent co-intercalation, which would cause the mpe to be around 100, would not cause the difference seen between the experimental and lithium values. The difference may be due to a small portion of lithium reacts with electrolytes that compose the surface film. During charging, the extracting process, at the first cycle, the experimental mpe is lighter than the mpe of lithium. It can be said that a small amount of the extracted lithium reacts with electrolytes that remain on the film. This accumulation continues through the 5th cycle. At the 50th cycle, of course, the measured mpe of the inserted and extracted pieces during the cycle are

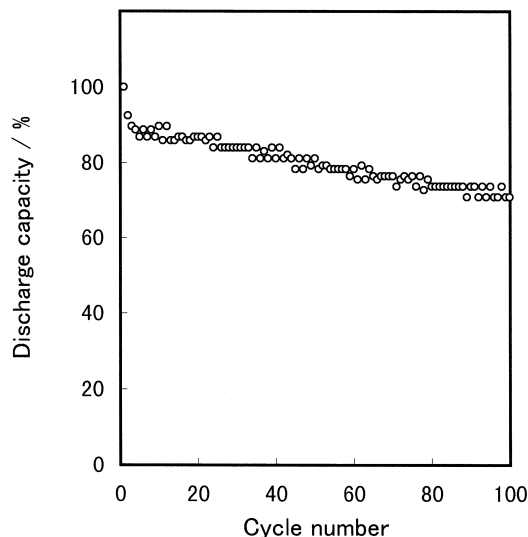


Fig. 5. Cycling performance of vanadium oxide film; current density: 0.04 mA cm^{-2} .

almost equal and in good agreement with the lithium value.

The cycling performance of a sputtered vanadium oxide film and the Δf at the frequency difference between the fully discharged condition of each cycle and the first cycle are shown in Figs. 5 and 6, respectively. The discharge capacity and Δf shows significant decrease during the first 5 cycles. The Δf decrease signifies an increase in the electrode mass. We consider this capacity loss to be caused by consumption a portion of the inserted lithium to make the surface film. Rough estimation of the mpe for the compound which composed the surface film is about 20, which is a value close to that of Li_2O , LiO_2 , LiOH and Li_2CO_3 (mpe = 15, 23, 24 and 37, respectively). During subsequent cycling, the capacity shows fairly good perfor-

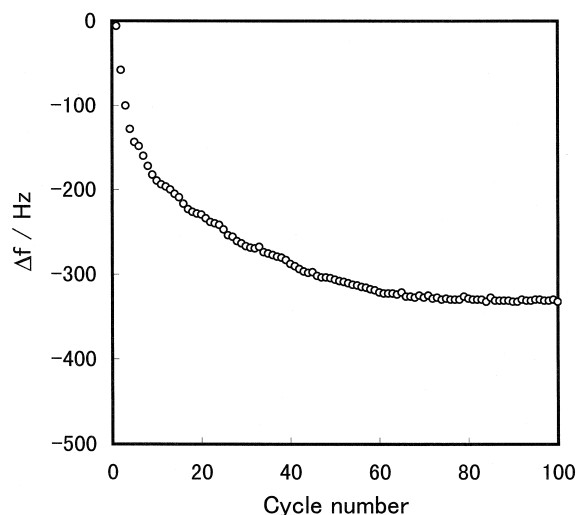


Fig. 6. Quartz resonance frequency change (Δf) at the fully charged condition of each cycle (Fig. 5).

mance. The Δf continuously decreases with the cycle repetition, which signifies an increase in the electrode mass during every cycle and indicates that some part of the inserted lithium can not be extracted. The surface morphology, as determined by SEM, does not significantly change after 100 cycles (not shown), but the EQCM results show a continuous net mass accumulation as the charge–discharge cycle is increased. This accumulation is clearly related to the origins of the reduced charging capacity of the cell.

4. Conclusions

In this work, we made orthorhombic V_2O_5 thin films by rf sputter deposition and demonstrated the lithium insertion and extraction. This film undergoes a reversible lithium insertion and extraction process. However, the charge–discharge profiles change into amorphous-like curves with repeated cycling caused by irreversible phase transformation. On the basis of our EQCM experiments, only lithium ions are successively inserted in and extracted from the V_2O_5 film over the repeated charge–discharge cycling. However, part of the inserted lithium irreversibly changes

the surface film during the first few cycles. In addition, a small amount of lithium molecules may survive in the V_2O_5 film following each cycle. It is clear that the remaining lithium ions on each successive charge–discharge cycle are responsible for the reduction in cell capacity.

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