Lithium intercalation into WO$_3$ and the phase diagram of Li$_x$WO$_3$

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We report studies of the electrochemical intercalation of lithium in WO$_3$ powder and in polycrystalline evaporated WO$_3$ films. Electrochemical cells with beryllium x-ray windows were used to study the structure changes in the WO$_3$ host in situ. Rietveld profile refinement was used to analyze the x-ray-diffraction patterns of Li$_x$WO$_3$ after correcting for the absorption of the beryllium window. Upon the intercalation of Li, the monoclinic structure of WO$_3$ proceeds to higher and higher symmetry. First a first-order phase transition to a tetragonal phase with $x<0.1$ in Li$_x$WO$_3$ occurs. Then another first-order phase transition to a cubic phase with $x<0.36$ occurs. The cubic phase can accommodate further Li, up to a maximum of about $x=0.5$. All the phase transitions can be reversed, although some hysteresis is observed; upon complete deintercalation, monoclinic WO$_3$ is recovered. We report the structural changes, prove that the transitions are first order, and give a phase diagram for Li$_x$WO$_3$ as a function of $x$. Our results suggest that the formation of the tetragonal phase upon intercalation of Li in WO$_3$ is responsible for the electrochromic properties of crystalline Li$_x$WO$_3$, and that conventional interpretations that ignore the existence of this phase are most likely in error.

INTRODUCTION

The intercalation of lithium in tungsten trioxide (WO$_3$) has been studied for many years.$^{1-4}$ Much of this work focused on the use of Li$_x$WO$_3$, prepared in an electrochemical cell, as an electrochromic. The success of such a device depends critically on the reversibility of the intercalation of Li in WO$_3$. We were surprised to find that no detailed studies of the structural changes occurring during the intercalation or deintercalation of Li in WO$_3$ have been made (to our knowledge). Therefore, we decided to make such a study to probe the reversibility of Li intercalation in WO$_3$.

In this work, lithium intercalation in WO$_3$ powders and polycrystalline films are reported. We studied both because films are conventionally used in electrochromic devices while our expertise is best suited to the study of powders. Nevertheless, our data on films are of high quality and are similar to the results on the powders.

Using the electrochemical methods, lithium was intercalated into the WO$_3$ powders and the films, and using in situ x-ray diffraction$^{5,6}$ the phase changes in the intercalated Li$_x$WO$_3$ were identified from the voltage curves and the x-ray data. The voltage of Li/Li$_x$WO$_3$ electrochemical cells measures the chemical potential of lithium in the Li$_x$WO$_3$. Since the chemical potentials of the components of coexisting phases (which occur at first-order transitions) are the same as the voltage, $V(x)$, of a Li battery plotted vs $x$ in Li$_x$WO$_3$, shows a plateau when two phases coexist. Such plateaus can be directly used to help determine phase-diagram information. Furthermore, the derivative, $-dV/dx$, shows peaks at the voltages and the compositions where the coexisting phases occur. Combining these electrochemical methods with in situ x-ray diffraction$^6$ gives a very powerful method for determining the phase diagram of intercalation compounds$^9$ which we apply here to Li$_x$WO$_3$.

The crystal structure of WO$_3$ is monoclinic at room temperature, with unit-cell dimensions: $a_M=7.306$ Å, $b_M=7.540$ Å, $c_M=7.692$ Å, and $\beta=90.881^\circ$. There are 8 tungsten and 24 oxygen atoms in each unit cell. (Since $\beta$ is close to 90°, the structure is pseudo-orthorhombic.) The structure is related to the cubic ReO$_3$ structure which has metal atoms on the corners of a simple-cubic lattice and oxygen atoms centered on every edge. As we will see, when Li intercalates into Li$_x$WO$_3$, the structure becomes successively more simple as $x$ increases. Figure 1 shows schematically the relation between the monoclinic cell of WO$_3$, the tetragonal cell of Li$_{0.1}$WO$_3$, and cubic (ReO$_3$-like) cell of Li$_{0.5}$WO$_3$.

EXPERIMENTS

The WO$_3$ powder used here was prepared by heating H$_2$WO$_4$ (99.5%, Aldrich) at 400 °C in air for 12 h accord-

FIG. 1. The relations of tetragonal and cubic-unit cells to the monoclinic unit cell.
ing to the following reaction:

$$\text{H}_2\text{WO}_4 \rightarrow \text{WO}_3 + \text{H}_2\text{O}.$$  \hspace{1cm} (1)

$\text{H}_2\text{WO}_4$ begins to decompose at about 200°C and $\text{WO}_3$ is obtained at above 250°C.11 Electrodes were prepared from this $\text{WO}_3$ powder using the methods described previously.12 Typical electrodes had an active mass of 20 mg, a coverage of 14 mg/cm$^2$ and a thickness of about 100 $\mu$m. The $\text{WO}_3$ films studied were evaporated on Al foil or on a Be foil substrate under a vacuum of about $1 \times 10^{-3}$ Torr. The as-evaporated $\text{WO}_3$ films were amorphous and became polycrystalline after subsequent annealing in air at 400°C for about 2 h. These $\text{WO}_3$ films were then directly used as electrodes.

Two-electrode electrochemical cells were used to intercalate Li in the $\text{WO}_3$ powder or into the film. Li foil (Lithium Corporation of America) was used as the anode and $\text{WO}_3$ powder electrodes or $\text{WO}_3$ film electrodes as the cathode. The electrolyte was a 1 molar solution of LiClO$_4$ dissolved in a 50:50 volume mixture of propylene carbonate and ethylene carbonate. The LiClO$_4$ salt was vacuum dried at 80°C for 24 h and the solvents were vacuum distilled prior to use.

Two types of electrochemical cells were used. Hermetically sealed test cells of the type described in Ref. 13 were used to determine the voltage, $V(x)$, of Li/Li$_x\text{WO}_3$ cells. Cells with Be x-ray windows8 (called x-ray cells here) were used to measure the structural changes in Li$_x\text{WO}_3$ in situ as $x$ was changed by charging and discharging the cells. Cu Kα radiation was used in all x-ray measurements. Our diffractometer uses the Bragg-Brentano geometry and has a diffracted beam monochromator.

To determine $V(x)$ and $-dx/dV$, cells were charged and discharged with constant currents between fixed voltage limits. The temperature of the cell was maintained constant in a thermostat to $\pm 0.1^\circ$C. Changes in $x$ are calculated from the cathode mass, the constant current, and the time of current flow. For a 20-mg electrode, a current of 23 $\mu$A gives a change $dx=1$ in Li$_x\text{WO}_3$ in 100 h. We call this current a 100-h rate for that electrode. Data were measured whenever $V$ changed by 0.005 V.

Two types of in situ x-ray experiments were carried out. A constant current was applied to an x-ray cell while a sequence of x-ray-diffraction profiles were continuously measured. This method allows for the rapid collection of data, but if the current is too large, nonequilibrium measurements are obtained. We used currents corresponding to a change $dx=1$ in 100 or 200 h where nonequilibrium effects are small. Alternatively, the cell voltage was fixed for about 24 h until the cell current decayed to a few microamperes; an x-ray profile was then collected of the equilibrium cathode.

X-ray patterns were analyzed by Rietveld profile refinement.14-17 The absorption from the beryllium window of the x-ray cell is angle dependent because of the Bragg-Brentano ($\theta$,2$\theta$) geometry we use. Before using the Rietveld program, the recorded intensity ($I$) from the x-ray cell was corrected using

$$I = I_0 \exp(2\mu l / \sin \theta),$$  \hspace{1cm} (2)

where $I_0$ is the diffracted intensity without beryllium absorption, $\mu$ is the absorption coefficient of the beryllium, $l$ is the thickness of beryllium foil, and $\theta$ is the diffraction angle. One measure of the success of the refinement is the Bragg $R_B$ factor defined as

$$R_B = \frac{\sum_{(h,k,l)} |I_o(h,k,l) - I_c(h,k,l)|}{\sum_{(h,k,l)} I_c(h,k,l)},$$  \hspace{1cm} (3)

where $I_o(h,k,l)$ is the observed peak $(h,k,l)$ intensity and $I_c(h,k,l)$ the calculated peak $(h,k,l)$ intensity. The sum goes over all $(h,k,l)$ peaks observed.

RESULTS

Figures 2(a) and 2(b) show the charge and discharge curves for Li/VO$_3$ cells with film and powder electrodes, respectively. Both materials have two plateaus during their discharge (intercalating Li) process. It will be proved later in this paper that the first plateau near 2.75 V during discharge corresponds to coexistence between monoclinic Li$_{1}\text{WO}_3$ and tetragonal Li$_{0.1}\text{WO}_3$. The second plateau near 2.5 V during discharge corresponds to coexistence between tetragonal Li$_{0.1}\text{WO}_3$ and cubic Li$_{0.3}\text{WO}_3$. The sloping regions in $V(x)$ near 3.0, 2.7 and 2.2 V correspond to three single-phase regions: monoclinic, tetragonal, and cubic in Li$_x\text{WO}_3$. The phase transitions are not as obvious during charge as during discharge, but are clearly observed when $-dx/dV$ is

FIG. 2. (a) Voltage vs $x$ for a Li/VO$_3$ film cell measured at 30°C. (b) Voltage vs $x$ for a Li/VO$_3$ powder cell. The solid curve is for the discharge of the cell and the dashed curve is for the charge of the cell. Two plateaus on the discharge curve correspond to the monoclinic (M) to tetragonal ($T$) phase change, and the tetragonal ($T$) to cubic ($C$) phase change.
plotted versus $V$. Figures 3(a) and 3(b) show $-dx/dV$ calculated from the data of Fig. 2. The derivative is obtained simply by taking $-\delta x/\delta V$ for adjacent data points. The peaks in Fig. 3 correspond to the plateaus in Fig. 2 and thus to the coexisting phase regions in Li$_x$WO$_3$. The features in Figs. 2 and 3 which correspond to the phase transitions are sharper for the powder. Presumably the crystallite size of the powder grains is larger than that of the grains in the film. Since finite-size effects are known to broaden first-order transition, we feel that the difference in crystallite size may explain the differences between the powder and the film. The range of stability of the three single phases, monoclinic, tetragonal, and cubic, are also indicated in Fig. 3.

The peaks in $-dx/dV$ suggest that Li$_x$WO$_3$ undergoes two reversible phase transitions during discharge and during charge. The broad peak observed near 2.65 V during charge is not associated with a phase transition but corresponds to capacity associated with deintercalation of Li from a single phase. We now report in situ x-ray results which show what these transitions and single-phase regions are. Since $V(x)$ and $-dx/dV$ vs $V$ for theWO$_3$ powder and theWO$_3$ film are almost the same, the results obtained from Li$_x$WO$_3$ powder will be presented and the results obtained from the film will be only quoted for comparison.

Figure 4 shows the x-ray-diffraction pattern for ourWO$_3$ powder. Since $a_M$, $b_M$, and $c_M$ all differ in length, the peaks (200), (020), and (002) near $23^\circ$ all appear at a different scattering angle. Figure 5 shows the x-ray profile obtained from an in situ x-ray cell discharged to 2.7 V with $x=0.095$ in Li$_x$WO$_3$. The triplet of peaks at $23^\circ$ in Fig. 4 is now a doublet. This suggests that two of the cell axes are now equivalent. We were able to index the pattern successfully using a tetragonal unit cell and proceeded to refine the structure in space group $P4/nmm-D_{1h}$. The refinement was successful giving $R_B=0.048$; Fig. 5 shows that the data and the calculation after refinement are in good agreement. With reference to Fig. 1, $c_T \sim \frac{1}{2}c_M$ and $a_T \sim \frac{1}{2}(a_M^2 + b_M^2)$. We measured $c_T=3.844$ Å and $a_T=5.203$ Å. Table I gives the final results of the refinement. Similar results were obtained for a Li/Li$_x$WO$_3$ cell with a film electrode. A cell fixed at 2.70 V gave $x=0.05$ in Li$_x$WO$_3$ (the value of $x$ for the tetragonal phase is smaller for the film compared to the powder—see Fig. 2) and could be refined using the same tetragonal structure as the powder except with $a_T=5.221$ Å and $c_T=3.862$ Å.

The x-ray cell with the powder electrode was discharged to 2.0 V which corresponded to $x=0.48$ in Li$_x$WO$_3$. Figure 6 shows the diffraction data for the cell. The doublet of peaks near $23^\circ$ in the tetragonal phase (Fig. 5) is now seen to be a single peak suggesting all three cell axes are equivalent. We were able to successfully index the pattern assuming a cubic structure with

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FIG. 4. X-ray diffraction pattern forWO$_3$ powder obtained by heating H$_2$WO$_4$ at 400°C in air. The Miller index is shown.

FIG. 5. X-ray-diffraction profile refinement for tetragonal Li$_x$WO$_3$ powder in an x-ray cell at $V'=2.7$ V; $x=0.095$ in Li$_x$WO$_3$. $+++$ are the x-ray data and the solid line (——) is the calculated profile. The structure parameters used in the calculation were from Table I. Beryllium peaks were excluded from the calculation.
TABLE I. Structure parameters for the tetragonal Li$_x$WO$_3$ powder. $x$ in Li$_x$WO$_3$: 0.095; space group: P4/mmm; cell dimensions: $a_1=5.203$ Å, $c_1=3.844$ Å; refined R factor: 0.048; and origin at 2/m.

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$a_c=3.729$ Å. Refinement in Pm3m was successful giving a Bragg R factor of $R_B=0.037$. Table II gives the results of the refinement. With reference to Fig. 1, we expect $a_2=(a_{20}+b_{20}+c_{20})/3$ as observed. The positions of the W and O atoms in Li$_{0.48}$WO$_3$ are the same as the Re and O atoms in ReO$_3$. The cubic phase was also found in a Li/Li$_2$WO$_3$ cell with a film electrode discharged to 2.0 V ($x=0.44$). The refined results were similar to those for the powder and the lattice constant was 3.726 Å for the film.

It remains to determine how the phase transitions between the monoclinic and tetragonal phases and between the tetragonal and cubic phases occur. An in situ x-ray experiment was performed to analyze the monoclinic $\rightarrow$ tetragonal phase transitions in Li$_x$WO$_3$. Figure 7(a) shows the charge and discharge curves for this in situ x-ray cell. Figure 7(b) shows the x-ray profiles taken at the points a, b, c, and d. Profile a in Figure 7(a) ($V=2.91$ V and $x=0.005$) corresponds to the monoclinic phase and d ($V=2.75$ V and $x=0.084$) predominantly to the tetragonal phase. It was found that all the other x-ray profiles obtained between 2.75 and 2.91 V ($x$ between 0.005 and 0.084) could be expressed by certain combinations of profile a and profile d in both charge and discharge processes indicating clearly that coexisting phases exist between $x \sim 0.01$ and 0.08. Figure 7(b) shows data measured at $a$, $b$, $c$, and $d$ and calculations made by combining profiles $a$ and $d$. To clearly see the results, only the x-ray profiles for $22^\circ < \theta < 25^\circ$ are plotted. Profile a shows the (002), (020), and (200) peaks in the monoclinic phase. In the tetragonal phase only two peaks appear in this region (see profile d). The thin solid lines in profile b and c are the raw experimental data and the thick dashed lines are linear combinations of profiles $a$ and $d$. These results prove that Li$_2$WO$_3$ undergoes a

FIG. 6. X-ray-diffraction profile refinement for cubic Li$_x$WO$_3$ powder in an x-ray cell at $V=2.0$ V; $x=0.48$ in Li$_x$WO$_3$. $+++\ldots$ are the x-ray data and the solid line (-----) is the calculated profile. The structure parameters used in the calculation were from Table II. Beryllium peaks were excluded from the calculation.

FIG. 7. (a) Voltage vs $x$ for the in situ x-ray cell charged and discharged between 3.2 and 2.75 V at a 200-h rate. The variation of $x$ in Li$_x$WO$_3$ within each x-ray profile was less than 0.02. The circles on the curves indicate the cell voltage and lithium composition in the Li$_x$WO$_3$ in the middle of each x-ray profile. (b) X-ray-diffraction profiles $a$, $b$, $c$, and $d$ correspond to circles $a$, $b$, $c$, and $d$ in (a). Profile a is monoclinic, d is tetragonal; profiles $b$ and $c$ are from the plateau region [see (a)] and can be expressed by linear combination of profiles $a$ and $d$. In profiles $b$ and $c$ the solid curves are raw x-ray data and the dashed curves are from the linear combination of profiles $a$ and $d$.
first-order phase transition from the monoclinic phase to the tetragonal phase as Li is intercalated since coexisting phases are observed.

Using the same methods, we analyzed the x-ray profiles corresponding to the tetragonal ↔ cubic phase transitions. A second in situ x-ray experiment was carried out using a constant current corresponding to a 100-h rate. Figure 8(a) shows $V(x)$ measured during discharge and charge for the second in situ x-ray cell. The circles on the curves indicate where the x-ray measurements were made. All 40 x-ray profiles were analyzed with the Rietveld profile refinement program. An x-ray profile obtained at $V = 2.65$ V and $x = 0.1$ [indicated by circle $a$ in Fig. 8(a)] showed the tetragonal structure [see pattern $a$ in Fig. 8(b)], and the x-ray profile obtained at 2.39 V and $x = 0.37$ [indicated by circle $d$ in Fig. 8(a)] showed the cubic phase [see profile $d$ in Fig. 8(b)]. All (eight) x-ray profiles measured in the tetragonal to cubic phase transition region (from 2.57 to 2.38 V) during the discharge can be expressed by certain linear combinations of tetragonal profile $a$ and cubic profile $d$. Figure 8(b) shows calculated profiles for points $b$ and $c$ collected in the plateau region during discharge as indicated by the circles in Fig. 8(a). The thin solid lines in Fig. 8(b) are the raw x-ray profiles, and the thick dashed lines are suitable linear combinations of profiles $a$ and $d$. The linear combinations and the raw data agree well. During charge, the lithium deintercalates from Li$_x$WO$_3$. All 11 x-ray patterns from $e'$ to $e$ in Fig. 8(a) showed cubic crystal structures, but the unit-cell dimension changed continuously. Figure 9 shows the cubic lattice constant plotted vs $x$ in Li$_x$WO$_3$ during deintercalation. Figure 9 shows that the volume of cubic unit cell shrinks as lithium is intercalated. The x-ray profiles corresponding to the cubic to tetragonal phase transition during the charge were also analyzed. Circles between $e$ and $g$ in Fig. 8(a) during the charge were analyzed with the same linear combination method used previously. All x-ray profiles from $e$ to $g$ could be fitted by a linear combination of profile $a$ and profile $e$. All phase transitions in Li$_x$WO$_3$ are first order, showing significant coexistence ranges.

Combining all the results discussed above, a phase diagram for electrochemically formed Li$_x$WO$_3$ powder at room temperature can be constructed. Figure 10 shows the phase diagram of Li$_x$WO$_3$. The phase diagram shows hysteresis between intercalation and deintercalation, especially concerning the range of cubic phase. During discharge (intercalation), Li$_x$WO$_3$ is cubic for $0.36 < x < 0.50$. During charge (deintercalation), Li$_x$WO$_3$ is cubic for $0.21 < x < 0.50$. Figure 9 shows that the cubic lattice constant of Li$_x$WO$_3$ during charge is ap-

![FIG. 8.](image1)  
FIG. 8. (a) Voltage vs $x$ for the second in situ x-ray cell charged and discharged between 3.2 and 2.0 V at a 100-h rate. Circles on the curves show the state of the x-ray cell in the middle of each x-ray pattern. (b) X-ray profiles $a$, $b$, $c$, and $d$ correspond to circles $a$, $b$, $c$, and $d$ in (a). Profile $a$ is tetragonal and profile $d$ is cubic. Profiles $b$ and $c$ are from the plateau region in discharge and can be expressed by a linear combination of tetragonal profile $a$ and cubic profile $d$.

![FIG. 10.](image2)  
FIG. 10. Phase diagram for electrochemically formed Li$_x$WO$_3$ at room temperature.
approximately constant for $0.36 < x < 0.50$, and then increases as $x$ decreases further. A similar phase diagram for the Li$_x$WO$_3$ film is expected, due to the similarities of $V(x)$ and $-dx/dV$.

**DISCUSSION AND CONCLUSION**

The crystal structures of electrochemically formed Li$_x$WO$_3$ and the correspondence of the plateaus of $V(x)$ of the Li/Li$_x$WO$_3$ cell with structural transitions were determined. The structures of monoclinic ($M$), tetragonal ($T$), and cubic ($C$) Li$_x$WO$_3$ phases are related as shown in Fig. 1 from which the relations of unit-cell dimensions are

$$a_M = 7.310 \text{Å},$$
$$b_M = 7.540 \text{Å},$$
$$c_M = 7.695 \text{Å},$$
$$\beta = 90.89^\circ,$$
$$a_T = 5.203 \text{Å} \approx \frac{1}{2}(a_M^2+b_M),$$
$$c_T = 3.844 \text{Å} \approx \frac{1}{2}c_M,$$
$$a_C = 3.729 \text{Å} \approx (a_M+b_M+c_M)/6 \quad \text{(for Li$_{0.37}$WO$_3$)}.$$  

The WO$_3$ host is formed by corner-shared WO$_6$ octahedra extending in three dimensions. The WO$_6$ octahedra zigzag in the WO$_3$ structure so a unit cell with eight W atoms must be chosen to show the lattice symmetry.

As lithium intercalates, the structure of the WO$_3$ host changes first to tetragonal symmetry. The zigzag of the octahedra in the $c$ direction disappears ($c_T = \frac{1}{2}c_M$) and the W-O bond lengths in the $a$ and $b$ directions become equal ($a_T = b_T$). There are two W atoms in the tetragonal unit cell.

With more intercalated lithium, the structure of the Li$_x$WO$_3$ host finally becomes cubic. The zigzags of the WO$_6$ octahedra disappear ($a_C \approx \frac{1}{2}a_M$, $b_M$, the $\frac{1}{2}c_M$), the W-O bond length becomes equal in all three directions, and there is a single W atom in the ReO$_3$-like unit cell. Figure 11 shows comparable unit-cell dimensions: $\frac{1}{2}a_M$, $b_M$, $\frac{1}{2}c_M$, $a_T/\sqrt{2}$, $c_T$, and $a_C$ for the three structures obtained in Li$_x$WO$_3$.

It is worthwhile to compare the unit-cell volumes of the monoclinic ($V_M$), tetragonal ($V_T$), and cubic ($V_C$) phases. Keeping the unit-cell relations in mind (see Fig. 1), we compare the values of $V_M/8$, $V_T/2$, and $V_C$ in Table III. The lattice dimensions of the Li$_x$WO$_3$ host shrink as lithium is added. The intercalated lithium atoms are located at interstitial sites (we do not know exactly where they are) and ionized at room temperature. The electron from the Li 2s level enters into the conduction band made up predominantly of W 5d orbitals. The Li$^+$ ions at interstitial positions may then attract the surrounding O$^{2-}$ ions in the lattice causing the lattice to contract.

Sleight and Gillson$^{18}$ have studied the solid solution series Re$_x$W$_{1-x}$O$_3$. They found that, for $x > 0.25$, the compound is isomorphous with ReO$_3$, i.e., cubic. Since Re has one more electron than W, this suggests that the charge transfer from Li to WO$_3$ is not the presence of the Li in the lattice, is responsible for the M$\leftrightarrow$T$\leftrightarrow$C phase transitions in WO$_3$. Sleight and Gillson did not investigate small Re concentrations so they did not find a tetragonal phase which may exist.

The charge transfer from Li to the WO$_3$ host is thought to move the Fermi level upward with respect to the bands in the rigid-band model. The rigid-band model only works well when the host does not change significantly as intercalant is added. As we have shown, the monoclinic phase of Li$_x$WO$_3$ is extremely narrow with $0 < x < 0.01$. Beyond $x = 0.01$, coexistence with the tetragonal phase occurs. Therefore, any interpretation of the electrochromic effects which occur in Li$_x$WO$_3$ must consider the physical properties of the tetragonal phase and must go beyond a simple interpretation of the rigid-band model.

**TABLE III.** The comparison of unit-cell volumes of three phases.

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$^*_{To whom correspondence should be sent.}$


