

## Lithium intercalation into $\text{WO}_3$ and the phase diagram of $\text{Li}_x\text{WO}_3$

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We report studies of the electrochemical intercalation of lithium in  $\text{WO}_3$  powder and in polycrystalline evaporated  $\text{WO}_3$  films. Electrochemical cells with beryllium x-ray windows were used to study the structure changes in the  $\text{WO}_3$  host *in situ*. Rietveld profile refinement was used to analyze the x-ray-diffraction patterns of  $\text{Li}_x\text{WO}_3$  after correcting for the absorption of the beryllium window. Upon the intercalation of Li, the monoclinic structure of  $\text{WO}_3$  proceeds to higher and higher symmetry. First a first-order phase transition to a tetragonal phase with  $x \sim 0.1$  in  $\text{Li}_x\text{WO}_3$  occurs. Then another first-order phase transition to a cubic phase with  $x \sim 0.36$  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  $\text{WO}_3$  is recovered. We report the structural changes, prove that the transitions are first order, and give a phase diagram for  $\text{Li}_x\text{WO}_3$  as a function of  $x$ . Our results suggest that the formation of the tetragonal phase upon intercalation of Li in  $\text{WO}_3$  is responsible for the electrochromatic properties of crystalline  $\text{Li}_x\text{WO}_3$ , and that conventional interpretations that ignore the existence of this phase are most likely in error.

### INTRODUCTION

The intercalation of lithium in tungsten trioxide ( $\text{WO}_3$ ) has been studied for many years.<sup>1-4</sup> Much of this work focused on the use of  $\text{Li}_x\text{WO}_3$ , 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  $\text{WO}_3$ . We were surprised to find that no detailed studies of the structural changes occurring during the intercalation or deintercalation of Li in  $\text{WO}_3$  have been made (to our knowledge). Therefore, we decided to make such a study to probe the reversibility of Li intercalation in  $\text{WO}_3$ .

In this work, lithium intercalation in  $\text{WO}_3$  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  $\text{WO}_3$  powders and the films, and using *in situ* x-ray diffraction,<sup>5,6</sup> the phase changes in the intercalated  $\text{Li}_x\text{WO}_3$  were identified from the voltage curves and the x-ray data. The voltage of  $\text{Li}/\text{Li}_x\text{WO}_3$  electrochemical cells measures the chemical potential of lithium in the  $\text{Li}_x\text{WO}_3$ .<sup>7</sup> 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  $\text{Li}_x\text{WO}_3$ , shows a plateau when two phases coexist. Such plateaus can be directly used to help determine phase-diagram information. Furthermore, the derivative,  $-dx/dV$ , shows peaks at the voltages and the compositions where the coexisting phases occur. Combining these electrochemical methods with *in situ* x-ray diffraction<sup>8</sup> gives a very powerful method for determining the phase diagram of intercalation com-

pounds<sup>9</sup> which we apply here to  $\text{Li}_x\text{WO}_3$ .

The crystal structure of  $\text{WO}_3$  is monoclinic at room temperature, with unit-cell dimensions:  $a_M=7.306 \text{ \AA}$ ,  $b_M=7.540 \text{ \AA}$ ,  $c_M=7.692 \text{ \AA}$ , and  $\beta=90.881^\circ$ .<sup>10</sup> There are 8 tungsten and 24 oxygen atoms in each unit cell. (Since  $\beta$  is close to  $90^\circ$ , the structure is pseudo-orthorhombic.) The structure is related to the cubic  $\text{ReO}_3$  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  $\text{Li}_x\text{WO}_3$ , the structure becomes successively more simple as  $x$  increases. Figure 1 shows schematically the relation between the monoclinic cell of  $\text{WO}_3$ , the tetragonal cell of  $\text{Li}_{0.1}\text{WO}_3$ , and cubic ( $\text{ReO}_3$ -like) cell of  $\text{Li}_{0.5}\text{WO}_3$ .

### EXPERIMENTS

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

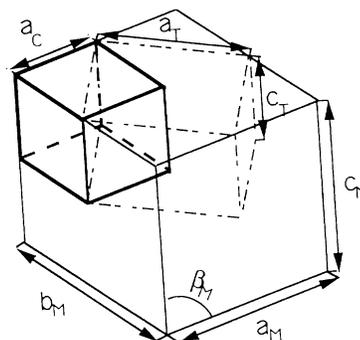
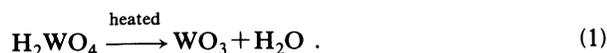


FIG. 1. The relations of tetragonal and cubic-unit cells to the monoclinic unit cell.

ing to the following reaction:



H<sub>2</sub>WO<sub>4</sub> begins to decompose at about 200 °C and WO<sub>3</sub> is obtained at above 250 °C.<sup>11</sup> Electrodes were prepared from this WO<sub>3</sub> powder using the methods described previously.<sup>12</sup> Typical electrodes had an active mass of 20 mg, a coverage of 14 mg/cm<sup>2</sup> and a thickness of about 100 μm. The WO<sub>3</sub> films studied were evaporated on Al foil or on a Be foil substrate under a vacuum of about 1 × 10<sup>-5</sup> Torr. The as-evaporated WO<sub>3</sub> films were amorphous and became polycrystalline after subsequent annealing in air at 400 °C for about 2 h. These WO<sub>3</sub> films were then directly used as electrodes.

Two-electrode electrochemical cells were used to intercalate Li in the WO<sub>3</sub> powder or into the film. Li foil (Lithium Corporation of America) was used as the anode and WO<sub>3</sub> powder electrodes or WO<sub>3</sub> film electrodes as the cathode. The electrolyte was a 1 molar solution of LiClO<sub>4</sub> dissolved in a 50:50 volume mixture of propylene carbonate and ethylene carbonate. The LiClO<sub>4</sub> 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<sub>x</sub>WO<sub>3</sub> cells. Cells with Be x-ray windows<sup>8</sup> (called x-ray cells here) were used to measure the structural changes in Li<sub>x</sub>WO<sub>3</sub> *in situ* as  $x$  was changed by charging and discharging the cells. Cu  $K\alpha$  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 ±0.1 °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 μA gives a change  $\delta x = 1$  in Li<sub>x</sub>WO<sub>3</sub> 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, non-equilibrium measurements are obtained. We used currents corresponding to a change  $\delta x = 1$  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.<sup>14-17</sup> 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 ( $I_r$ ) from the x-ray cell was corrected using

$$I_o = I_r \exp(2\mu l / \sin\theta) , \quad (2)$$

where  $I_o$  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

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

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/WO<sub>3</sub> 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<sub>x</sub>WO<sub>3</sub> and tetragonal Li<sub>0.1</sub>WO<sub>3</sub>. The second plateau near 2.5 V during discharge corresponds to coexistence between tetragonal Li<sub>0.1</sub>WO<sub>3</sub> and cubic Li<sub>0.36</sub>WO<sub>3</sub>. 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<sub>x</sub>WO<sub>3</sub>. The phase transitions are not as obvious during charge as during discharge, but are clearly observed when  $-dx/dV$  is

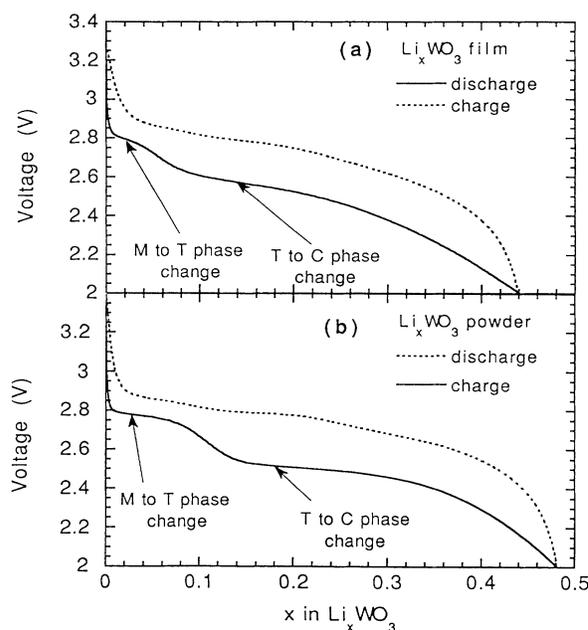


FIG. 2. (a) Voltage vs  $x$  for a Li/WO<sub>3</sub> film cell measured at 30 °C. (b) Voltage vs  $x$  for a Li/WO<sub>3</sub> powder cell. The solid curve is for the discharge of the cell and the dashed curve is for the charge of the cell. Two plateaus on the discharge curve correspond to the monoclinic ( $M$ ) 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  $\text{Li}_x\text{WO}_3$ . 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  $\text{Li}_x\text{WO}_3$  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 the  $\text{WO}_3$  powder and the  $\text{WO}_3$  film are almost the same, the results obtained from  $\text{Li}_x\text{WO}_3$  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 our  $\text{WO}_3$  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  $\text{Li}_x\text{WO}_3$ . The triplet of peaks at  $23^\circ$  in Fig. 4 is now a doublet. This suggests that two of

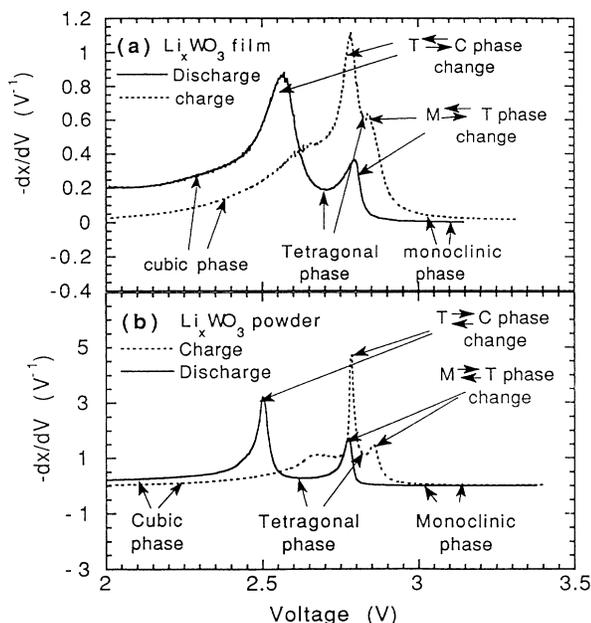


FIG. 3. (a) Derivative  $-(dx/dV)_T$  vs  $V$  computed from data of Fig. 2(a). The derivative data in (b) correspond to the data of the  $\text{WO}_3$  powder cell from Fig. 2. (b) The peaks in the derivative correspond to the plateaus in Fig. 2.

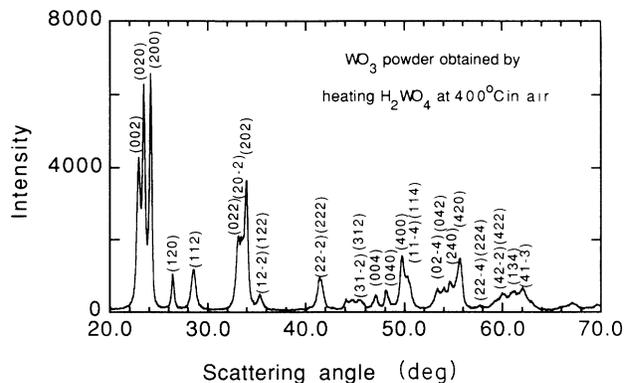


FIG. 4. X-ray diffraction pattern for  $\text{WO}_3$  powder obtained by heating  $\text{H}_2\text{WO}_4$  at  $400^\circ\text{C}$  in air. The Miller index is shown.

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  $P4/nmm-D_{4h}^7$ . 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  $a_T \sim \frac{1}{2}\sqrt{(a_M^2 + b_M^2)}$ . We measured  $c_T=3.844 \text{ \AA}$  and  $a_T=5.203 \text{ \AA}$ . Table I gives the final results of the refinement. Similar results were obtained for a  $\text{Li}/\text{Li}_x\text{WO}_3$  cell with a film electrode. A cell fixed at 2.70 V gave  $x=0.05$  in  $\text{Li}_x\text{WO}_3$  (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  $a_T=5.221 \text{ \AA}$  and  $c_T=3.862 \text{ \AA}$ .

The x-ray cell with the powder electrode was discharged to 2.0 V which corresponded to  $x=0.48$  in  $\text{Li}_x\text{WO}_3$ . 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

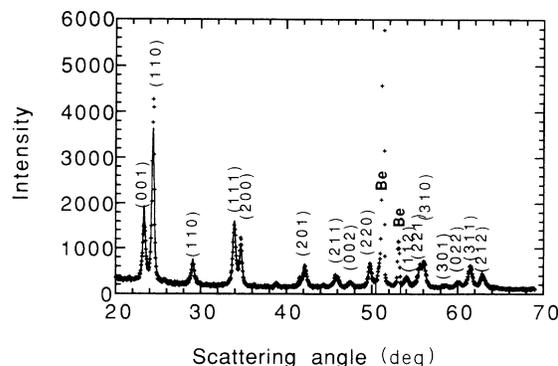


FIG. 5. X-ray-diffraction profile refinement for tetragonal  $\text{Li}_x\text{WO}_3$  powder in an x-ray cell at  $V=2.7 \text{ V}$ ;  $x=0.095$  in  $\text{Li}_x\text{WO}_3$ . +++ are the x-ray data and the solid line (—) is the calculated profile. The structure parameters used in the calculation were from Table I. Beryllium peaks were excluded from the calculation.

TABLE I. Structure parameters for the tetragonal  $\text{Li}_x\text{WO}_3$  powder.  $x$  in  $\text{Li}_x\text{WO}_3$ : 0.095; space group:  $P4/nmm$ ; cell dimensions:  $a_T=5.203$  Å,  $c_T=3.844$  Å; refined  $R$  factor: 0.048; and origin at  $2/m$ .

	$x$	$y$	$z$	$B$
W1	0.25	0.25	0.432	1.0
W2	0.75	0.75	0.568	1.0
O1	0.25	0.25	0.932	4.8
O2	0.75	0.75	0.068	4.8
O3	0.00	0.00	0.50	4.8
O4	0.50	0.50	0.50	4.8
O5	0.50	0.00	0.50	4.8
O6	0.00	0.50	0.50	4.8

$a_C=3.729$  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  $a_C \sim \frac{1}{2}(a_M + b_M + c_M)/3$  as observed. The positions of the W and O atoms in  $\text{Li}_{0.48}\text{WO}_3$  are the same as the Re and O atoms in  $\text{ReO}_3$ . The cubic phase was also found in a  $\text{Li}/\text{Li}_x\text{WO}_3$  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  $\leftrightarrow$  tetragonal phase transitions in  $\text{Li}_x\text{WO}_3$ . 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) (at  $V=2.91$  V and  $x=0.005$ ) corresponds to the monoclinic phase and  $d$  (at  $V=2.75$  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

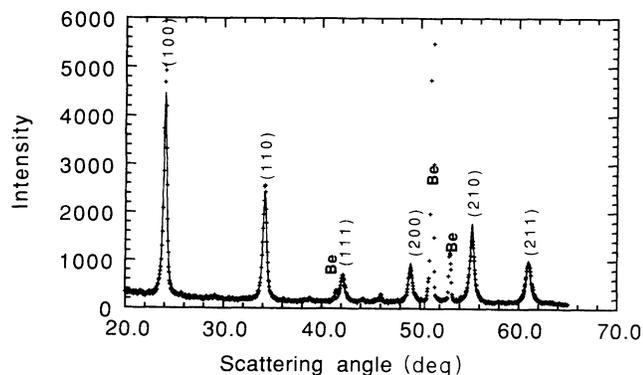


FIG. 6. X-ray-diffraction profile refinement for cubic  $\text{Li}_x\text{WO}_3$  powder in an x-ray cell at  $V=2.0$  V;  $x=0.48$  in  $\text{Li}_x\text{WO}_3$ . +++ are the x-ray data and the solid line (—) is the calculated profile. The structure parameters used in the calculation were from Table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

Table II. Structure parameters for cubic  $\text{Li}_x\text{WO}_3$  powder.  $x$  in  $\text{Li}_x\text{WO}_3$ : 0.48; space group:  $Pm3m$ ; cell dimension:  $a_C=3.729$  Å; refined  $R$  factor: 0.037; and origin at  $m3m$ .

	$x$	$y$	$z$	$B$
W	0.00	0.00	0.00	0.8
O(1)	0.50	0.00	0.00	1.0
O(2)	0.00	0.50	0.00	1.0
O(3)	0.00	0.00	0.50	1.0

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  $22^\circ < 2\theta < 25^\circ$  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  $\text{Li}_x\text{WO}_3$  undergoes a

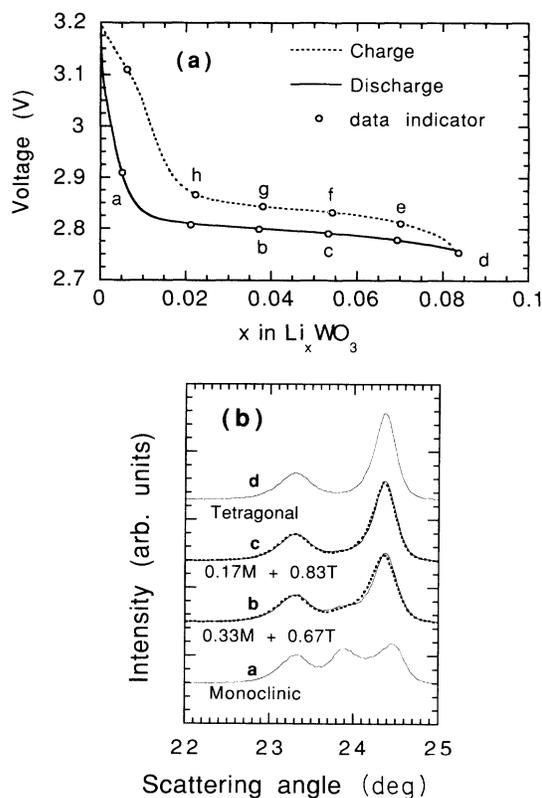


FIG. 7. (a) Voltage vs  $x$  for the *in situ* x-ray cell charged and discharged between 3.2 and 2.75 V at a 200-h rate. The variation of  $x$  in  $\text{Li}_x\text{WO}_3$  within each x-ray profile was less than 0.02. The circles on the curves indicate the cell voltage and lithium composition in the  $\text{Li}_x\text{WO}_3$  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  $\leftrightarrow$  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 combina-

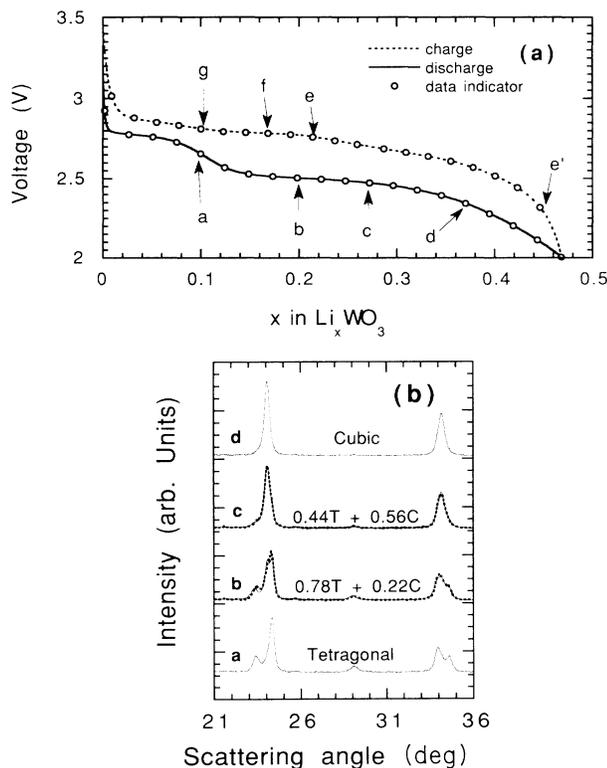


FIG. 8. (a) Voltage vs  $x$  for the second *in situ* x-ray cell charged and discharged between 3.2 and 2.0 V at a 100-h rate. Circles on the curves show the state of the x-ray cell in the middle of each x-ray pattern. (b) X-ray profiles *a*, *b*, *c*, and *d* correspond to circles *a*, *b*, *c*, and *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*.

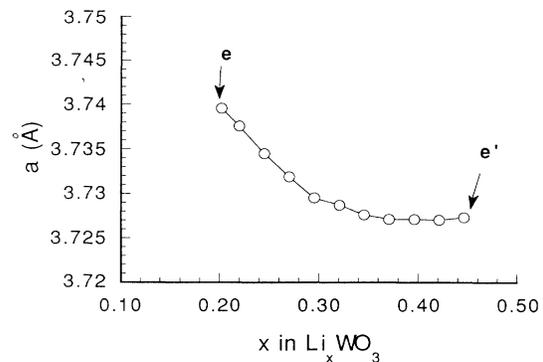


FIG. 9. The cubic unit-cell axis,  $a_c$  vs  $x$  in  $\text{Li}_x\text{WO}_3$  during lithium deintercalation in the cubic phase.

tions of profiles *a* and *d*. The linear combinations and the raw data agree well. During charge, the lithium deintercalates from  $\text{Li}_x\text{WO}_3$ . 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  $\text{Li}_x\text{WO}_3$  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  $\text{Li}_x\text{WO}_3$  are first order, showing significant coexistence ranges.

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

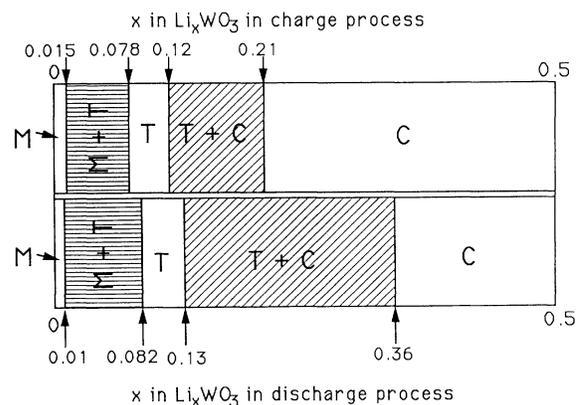


FIG. 10. Phase diagram for electrochemically formed  $\text{Li}_x\text{WO}_3$  at room temperature.

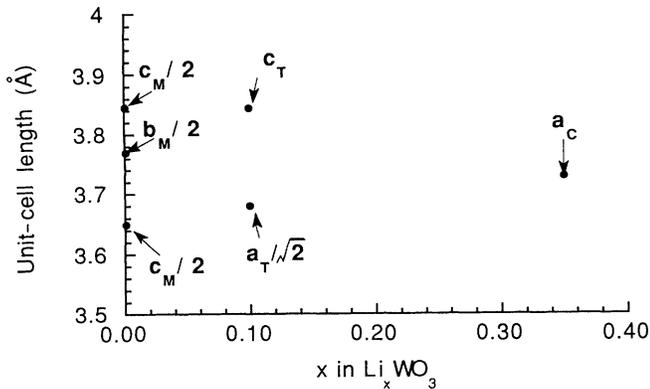


FIG. 11. Comparison of the unit-cell dimensions among three phases.

proximately constant for  $0.36 < x < 0.50$ , and then increases as  $x$  decreases further. A similar phase diagram for the  $\text{Li}_x\text{WO}_3$  film is expected, due to the similarities of  $V(x)$  and  $-dx/dV$ .

#### DISCUSSION AND CONCLUSION

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

$$\begin{aligned} a_M &= 7.310 \text{ \AA} , \\ b_M &= 7.540 \text{ \AA} , \\ c_M &= 7.695 \text{ \AA} , \end{aligned} \quad (4)$$

$$\begin{aligned} \beta &= 90.89^\circ , \\ a_T &= 5.203 \text{ \AA} \sim \frac{1}{2} \sqrt{(a_M^2 + b_M^2)} , \\ c_T &= 3.844 \text{ \AA} \sim \frac{1}{2} c_M , \end{aligned} \quad (5)$$

$$a_C = 3.729 \text{ \AA} \sim (a_M + b_M + c_M)/6 \quad (\text{for } \text{Li}_{0.37}\text{WO}_3) . \quad (6)$$

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

As lithium intercalates, the structure of the  $\text{WO}_3$  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.

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

Phase	Unit-cell volume ( $\text{\AA}^3$ )	Comparison ( $\text{\AA}^3$ )
Monoclinic $\text{WO}_3$	$V_M = 424.1$	$V_M/8 = 53.01$
Tetragonal $\text{Li}_x\text{WO}_3$	$V_T = 104.3$	$V_T/2 = 52.15$
Cubic $\text{Li}_x\text{WO}_3$	$V_C = 51.73$	$V_C = 51.73$

With more intercalated lithium, the structure of the  $\text{Li}_x\text{WO}_3$  host finally becomes cubic. The zigzags of the  $\text{WO}_6$  octahedra disappear ( $a_C \sim \frac{1}{2}a_M$ ,  $\frac{1}{2}b_M$ , 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  $\text{ReO}_3$ -like unit cell. Figure 11 shows comparable unit-cell dimensions:  $\frac{1}{2}a_M$ ,  $\frac{1}{2}b_M$ ,  $\frac{1}{2}c_M$ ,  $a_T/\sqrt{2}$ ,  $c_T$ , and  $a_C$  for the three structures obtained in  $\text{Li}_x\text{WO}_3$ .

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  $\text{Li}_x\text{WO}_3$  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  $\text{Li}^+$  ions at interstitial positions may then attract the surrounding  $\text{O}^{2-}$  ions in the lattice causing the lattice to contract.

Sleight and Gillson<sup>18</sup> have studied the solid solution series  $\text{Re}_2\text{W}_{1-z}\text{O}_3$ . They found that, for  $z > 0.25$ , the compound is isostructural with  $\text{ReO}_3$ , i.e., cubic. Since Re has one more electron than W, this suggests that the charge transfer from Li to  $\text{WO}_3$ , not the presence of the Li in the lattice, is responsible for the  $M \leftrightarrow T \leftrightarrow C$  phase transitions in  $\text{WO}_3$ . 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  $\text{WO}_3$  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  $\text{Li}_x\text{WO}_3$  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  $\text{Li}_x\text{WO}_3$  must consider the physical properties of the tetragonal phase and must go beyond a simple interpretation of the rigid-band model.

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