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Experiment 8

Hydrogen Insertion into WO_3

M. Stanley Whittingham

Notes for Instructors

Purpose

To reductively insert protons into solid tungsten trioxide and observe the effect on color and conductivity.

Method

If yellow–green WO_3 is placed in a beaker and hydrochloric acid is added to it, nothing happens. But if a few chips of zinc are added, hydrogen is produced, causing the solid to turn a very dark blue in a chemical reduction. Its electrical conductivity also increases dramatically, from less than 10^{-6} /Ω-cm to around 10^{-2} /Ω-cm. The color and conductivity changes observed are due to the intercalation of hydrogen atoms into the cavities in the WO_3 structure, and the donation of their electrons to the conduction band of the WO_3 matrix, making H_xWO_3. These electrons make the material behave like a semiconductor, and at higher values of x, a metal. If the H_xWO_3 is left exposed to the air, it will re-oxidize and return to its original yellow–green color.

$$\underset{\text{Yellow–green}}{WO_3} \overset{Zn + HCl}{\underset{O_2}{\rightleftarrows}} \underset{\text{Blue}}{H_xWO_3}$$

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Materials

Tungsten trioxide, WO_3 (Aldrich, 99%+; Johnson–Matthey 99.8%)

3 M HCl

Zinc metal (filings)

Filter paper, Büchner funnel, suction flask, and water aspirator

Glass capillary tubes, 1.5 × 100 mm (melting point size)

18-gauge copper wire

Ohmmeter

Rubber band

Answers to Warm-up Exercises

$$Zn + 2H^+ \rightarrow H_2 + Zn^{2+}$$

$$WO_3 + \frac{x}{2} H_2 \rightarrow H_xWO_3$$

$$4H_xWO_3 + xO_2 \rightarrow 4WO_3 + 2xH_2O$$

Hydrogen Insertion into WO_3

Purpose

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Introduction

Tungsten trioxide has an idealized structure consisting of WO_6 octahedra joined at their corners. It may also be considered as having the perovskite structure of $CaTiO_3$ with all of the calcium sites (in the center of the unit cell shown in Figure 1) vacant. When an atom is inserted into the center of the WO_3 structure, the structure is called a tungsten bronze.

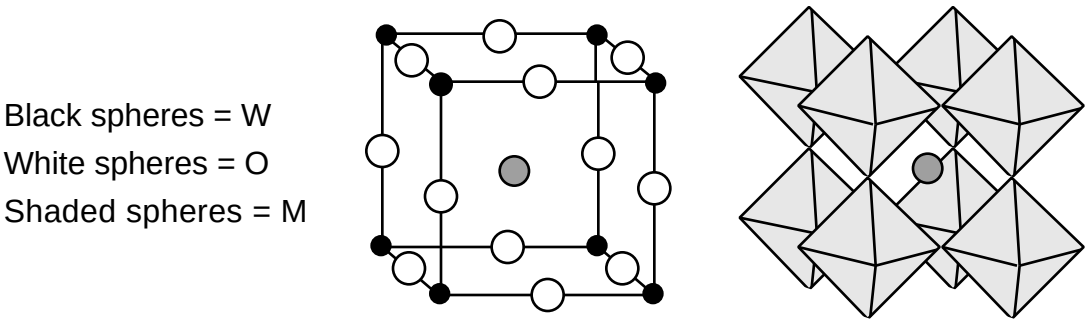

Figure 1. Two views of the idealized M_xWO_3 unit cell.

These compounds have the formula M_xWO_3, where M is usually Na or K and $0 < x < 1$. The color of the compound is controlled by the stoichiometry; thus $Na_{0.9}WO_3$ is yellow, but $Na_{0.3}WO_3$ is blue–black (*see* Figure 2). The intense colors of these solids have led to their use in paint pigments.

M can be an alkali metal, Ca, Sr, Ba, Al, In, Tl, Sn, Pb, Cu, Ag, Cd, the rare earth elements, H^+, or NH_4^+. In this experiment, you are going to make H_xWO_3.

The intercalation of hydrogen atoms into the cavities in the WO_3 structure and the donation of their electrons to the conduction band of the WO_3 matrix will cause color and conductivity changes. These electrons make the material behave like a metal, with both its conductivity and color being derived from free electron behavior. This coloration reaction is now being used in electrochromic displays for sunglasses and rear-view mirrors in cars, and has been proposed for adjusting the transmission of

NOTE: This experiment was written by M. Stanley Whittingham, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY, 19302.

light through the glass panes in large buildings. In these applications the redox coloring reaction is carried out electrochemically.

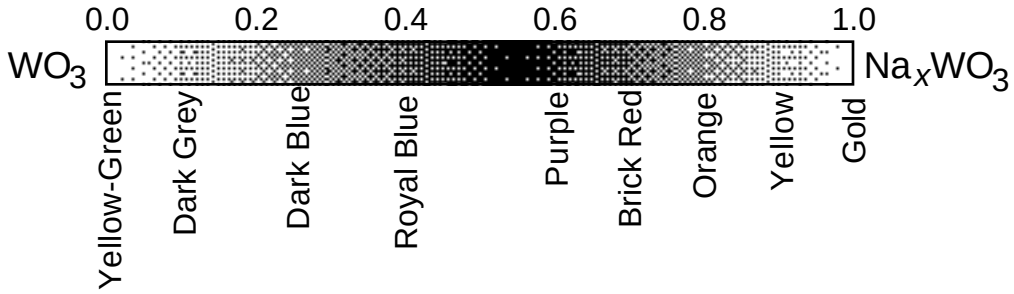

Figure 2. Change in color of Na_xWO_3 as x (shown at the top) varies.

Warm-up Exercises

Balance the equations.

a. $Zn + 2H^+ \rightarrow H_2 +$

b. $WO_3 + \frac{x}{2} H_2 \rightarrow$

c. $H_xWO_3 + xO_2 \rightarrow$

Procedure

Wear eye protection.

Synthesis

Place 0.5 g of WO_3 into a 150-mL beaker. **CAUTION: WO_3 is an irritant. Avoid creating or breathing dust. Avoid eye and skin contact. Wash hands thoroughly after handling.** What is the color of WO_3? Carefully pour about 50 mL of 3 M hydrochloric acid onto the WO_3. Does anything happen? Add less than 1 g of zinc filings to the acid and observe what takes place. **CAUTION: Keep hydrogen away from open flames.**

After all reaction has ceased, note the colors of all the products. Suction-filter off the solid product. Wash twice with water and air-dry for a few minutes.

Change in Conductivity upon Intercalation

Make a tube to measure the conductivity of WO_3 by first inserting a straight piece of copper wire (18-gauge) into a glass capillary tube, as

shown in Figure 3. The fit should be tight. Push the open end of the tube into some WO_3 so that some of the material is stuck in the tube. Flip the tube upside down and tap the copper wire end against a hard surface so that the WO_3 falls to the wire. Repeat this until there is about 1 cm of the material in the tube. Finally, insert another length of copper wire into the open end of the glass capillary, so the WO_3 is packed between the two copper electrodes. In order to ensure a tightly packed tube, carefully bend the copper wire electrodes and place a rubber band around the electrodes:

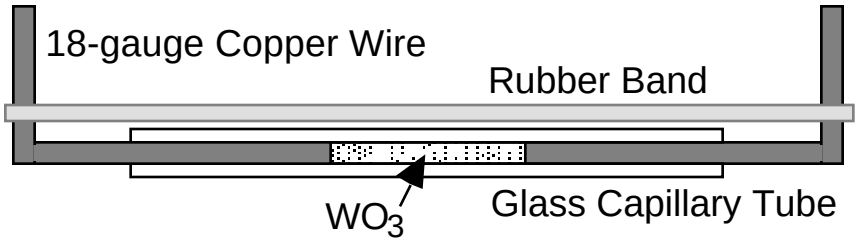

Figure 3. The apparatus used to measure the conductivity of WO_3 and H_xWO_3.

Prepare a similar tube packed with H_xWO_3. Make sure that the length of the sample in the tube is about the same.

Using an ohmmeter (adjust the meter to read in the 10–100-kΩ range), measure the electrical resistance between the electrodes of the WO_3 sample. Repeat the measurement on the H_xWO_3 sample. How much difference is there?

Re-oxidation of H_xWO_3 upon Exposure to Oxygen in the Air

Has the color of your sample changed at all since you made it? Leave your sample in your lab drawer for 1 week, then measure the conductivity again.

What happens when you leave H_xWO_3 exposed to the air? Does the conductivity change? Why?

Cleanup

Place the glass capillaries containing WO_3 and H_xWO_3, as well as any remaining solid, in an appropriately labeled waste container.