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# HUMIDITY SENSOR USING POTASSIUM HEXAGONAL TUNGSTEN BRONZE SYNTHESIZED FROM PEROXO-POLYTUNGSTIC ACID AND ITS RESISTIVITY CHANGE MECHANISM

Isao Tsuyumoto and Tetsuichi Kudo Institute of Industrial Science, University of Tokyo 7-22-1 Roppongi, Tokyo 106, Japan

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## ABSTRACT

We have found that potassium hexagonal tungsten bronze (K-HTB) synthesized from potassium peroxo-polytungstate at low temperature (500°C) shows a remarkable increase in resistivity in a humid atmosphere at room temperature. The mechanism of the resistivity increase by incorporation of water was investigated by gravimetry, complex impedance spectroscopy, and powder XRD measurement. The powder XRD profiles indicated that superlattice structure of the K-HTB emerges by incorporation of water. A layer structure model of the K-HTB was suggested from these results.

MATERIALS INDEX: tungsten, potassium, oxide, polyacid

### INTRODUCTION

In recent years there has been a great deal of interest in the use of precursors for the formation of inorganic materials (1). The sol-gel techniques based on hydrolysis and condensation of metal alkoxide is a typical example of such formation. The synthesis of a hexagonal form of tungsten trioxide from a hydrothermally prepared precursor ( $3WO_3 \cdot H_2O$ ) is pointed out as an instance close to the present study (2). Such synthetic routes generally have the advantages over conventional ones in that they enable us to synthesize



various metastable phases because of lower formation temperatures and better compositional uniformity of products. Moreover, special properties can be expected of substances formed at low temperatures because defect structures are often different from those of high temperature formation even though the basical structures are the same. Materials synthesis on such concepts is called "soft chemistry" or "chimie douce" (3).

We have reported that various tungstates with a defective hexagonal or pyrochlore type framework are synthesized through a soft chemical route using precursors precipitated from a peroxo-polytungstic acid (IPA) solution with alkaline or alkaline earth halides (4,5). It has also been shown that tungsten bronze phases with the same framework are formed



FIG. 3 Resistivity increase of the K-HTB at room temperature when  $P_{H_{2O}}$  was increased stepwise (DC 4-probe measurement).



#### FIG. 4.

Resistivity decrease of the K-HTB at room temperature when  $P_{H_{2O}}$  was decreased stepwise (DC 4-probe measurement).

at relatively low temperature  $(500 \sim 700 \circ C)$  by heating such precursors in a reducing atmosphere (H<sub>2</sub> 10%) (6). Of these, pyrochlore-type Cs<sub>x</sub>WO<sub>3</sub> is a new bronze synthesized for the first time by this low temperature synthetic process (7).

Potassium hexagonal tungsten bronze (K-HTB, K  $_{x}$ WO<sub>3</sub>; x  $\approx$  0.3) thus synthesized at 500°C is not different in basical crystal structure from conventional K-HTB synthesized by well-known solid state reaction around 1000°C (8). However, we have found that it shows a remarkable increase in resistivity by water incorporation (6). A fresh water-free sample pellet of the present K-HTB shows resistivity as low as 0.1  $\Omega cm$  at room temperature in a dry atmosphere like the conventional ones. However, its resistivity was dramatically increased in a humid atmosphere at room temperature (Fig. 1). At the same time, a significant amount of water incorporation by the sample pellet was gravimetrically observed (Fig. 2). It was also found that the present K-HTB shows a property as a humidity sensor in the  $P_{H_{2}O}$  range of 2.0x10<sup>-3</sup>~14.6 mmHg at room temperature (9,10). The resistivity of the sample pellet was increased in response to stepwise increases in  $P_{HO}$  as shown in Fig. 3, showing a clear equilibrium value of resistivity for each value of  $P_{H_{2}O}$ . For stepwise decreases in  $P_{H_{2O}}$ , its resistivity was decreased as shown in Fig. 4, indicating good reversibility. Infrared spectroscopic observations and density measurements have indicated that this unusual property is associated with the defect structure due to low temperature formation. The purpose of this paper is to investigate the mechanism of resistivity increase by water incorporation.

#### EXPERIMENT

<u>Synthetic Procedure</u>. Peroxo-polytungstic acid was prepared according to the previously reported method (11). Metallic W was dissolved in 15%  $H_2O_2aq$  to yield a pale yellow acidic solution. It was then dried at room temperature after removing excess  $H_2O_2$  catalytically with a platinized Pt net, resulting in a yellow glassy substance (IPA) with an approximate empirical formula of  $2WO_3 \cdot H_2O_2 \cdot 2H_2O_2$ .

White amorphous substance was precipitated by adding 50 ml of an IPA solution (1.2 mol/l as to tungsten) into 50 ml of a KBr solution (1.2 mol/l) with stirring. After storage for 24 h at 20 °C, the precipitate was filtered, rinsed with water, and then dried at 70 °C. Heating thus formed potassium peroxo-polytungstate in H<sub>2</sub> 10% (N<sub>2</sub> balance) at 500 °C for 1 h, dark blue potassium hexagonal tungsten bronze (K-HTB) was obtained (10).

<u>Gravimetry</u>. Gravimetry of K-HTB at different  $P_{H_2O}$  was carried out at room temperature using high sensitive balance (Cahn 2000 Recording Electrobalance) to investigate the relationship between  $P_{H_2O}$  and n (n in K<sub>x</sub>WO<sub>3</sub>·nH<sub>2</sub>O). The desired  $P_{H_2O}$  was made by mixing a dry gas with a wet one using mass flow controllers.

<u>Impedance Spectroscopy</u>. The changes of complex impedance of the present K-HTB by water incorporation were measured using impedance analyzer (Hewlett-Packard 4192A) with the oscillation level of 0.300 V over a frequency range of 5 Hz-13 MHz. The sample pellet of K-HTB was fabricated as follows. The powder sample of K-HTB was pressed at  $3x10^7$  Pa for 1 min into a pellet with 2.5 mm in diameter and 2 mm in thickness. After the gold electrodes were coated on both sides with gold paste (Tokuriki Chemical Corporation No. 8570), this pellet was reheated at the same condition as the synthesis for 1 h. The final

porosity of this sample pellet was ca. 35%. The changes of complex impedance in a wet atmosphere ( $P_{H20} = 11 \text{ mmHg}, 28^{\circ}\text{C}$ ) were measured using this sample pellet.

<u>Structural Analysis</u>. Structural change by incorporation of water was investigated by powder XRD measurement using monochromatized Cu  $K_a$  radiation. The 2  $\theta$  scanning was carried out stepwise with the width of 0.02° and the measuring time of 0.6 sec. In order to diminish preferred orientation, the sample was well ground and attached softly on a sample holder.

XRD spectra were taken using three types of powder samples: (a) taken immediately after reheating (water-free), (b) left in a wet atmosphere (R.H. 100%) for 67 hours, and (c) left in a wet atmosphere (R.H. 100%) for 113 hours.

#### **RESULTS AND DISCUSSION**

<u>Relationship between Water Vapor Pressure and Water Content</u>. Relationship between water content in the K-HTB and water vapor pressure was investigated by gravimetric analysis. Water content n (in K<sub>x</sub>WO<sub>3</sub>·nH<sub>2</sub>O) was increased stepwise in response to increase in water vapor pressure  $P_{H_2O}$ , showing a clear equilibrium value of n as shown in Fig. 5. Relationship between  $P_{H_2O}$  and the equilibrium value of n is shown in Fig. 6. The value of n equilibrium with the dry gas ( $P_{H_2O} = 2.0 \times 10^{-3}$  mmHg) was ca. 0.16. When used as a humidity sensor at room temperature, water molecules are assumed to adsorb and desorb the sites n>ca. 0.16. From TG and TPD spectrum it was found that water desorption occurs in two steps: one is r.t. ~ ca. 120°C in the range of n>ca. 0.12 and the other over ca. 120°C in the range of  $n = 0 \sim$  ca. 0.12 (6,10). An approximate theoretical fitting to the TG spectrum indicated that adsorption sites in K-HTB consists of two types, one of which has the adsorption energy ca. -50~-40 kJ/mol and the other ca. -10 kJ/mol (10). We can conclude that water adsorption sites of the K-HTB consist of two types with different adsorption energy. In this paper we discuss thermodynamics using the n vs.  $P_{H_2O}$ relationship at constant temperature.



FIG. 5 Increase of water content when  $P_{H_{2O}}$  was increased stepwise.



FIG. 6 Relationship between  $P_{H_2O}$  and the equilibrium value of water content n (in K<sub>x</sub>WO <sub>3</sub>·nH<sub>2</sub>O).

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Let us first discuss the *n* vs.  $P_{H_2O}$  relationship theoretically when the adsorption sites for H<sub>2</sub>O consist of two types. If the site energy of adsorption sites (site 1 and site 2) are  $E_1$  and  $E_2$  ( $E_1 < E_2 < 0$ ), respectively, the Helmholtz free energy F(n) of the K-HTB with water content *n* is

$$F(n) = E_1 n_1 + kT \ln N_1 C n_1 + E_2 n_2 + kT \ln N_2 C n_2$$
(1)

where  $n_1$  and  $n_2$  are the molar number of H<sub>2</sub>O distributed to site 1 and site 2, and *n* the total molar number of adsorbed H<sub>2</sub>O; therefore,

$$n=n_1+n_2 \tag{2}$$

 $N_1$  and  $N_2$  are the maximum accommodation number of site 1 and site 2, the mole of the adsorption host.

The adsorbed  $H_2O$  molecules are distributed over the two sites so as to minimize the Helmholtz free energy F(n). We can find  $n_1$  and  $n_2$  by using the Lagrange undetermined multiplier under the condition of [2].

$$\partial F/\partial n_1 = \partial F/\partial n_2 = \lambda \tag{3}$$

where  $\lambda$  is an undetermined multiplier and its value is related to the chemical potential  $\mu H_2O$  as follows:

$$\lambda = \partial F/\partial n_1 = \partial F/\partial n_2 = \mu H_2 O = \mu H_2 O^\circ + kT \ln P_{H_2 O}$$
(4)

Substituting [1] in [4], we obtain

$$\mu H_2 O = \mu H_2 O^\circ + kT \ln P_{H_2 O} = E_1 + kT \ln x_1 / (1 - x_1)$$
(5)

$$= E_2 + kT \ln x_2 / (1 - x_2) \tag{6}$$

where  $x_1$  and  $x_2$  are the occupancies of site 1 and site 2

$$x_1 = n_1 / N_1, x_2 = n_2 / N_2 \tag{7}$$

By transforming [5] and [6], the equation for the Langmuir adsorption isotherm is derived:

$$x_i = K P_{H_2O} / (1 + K P_{H_2O})$$
(8)

$$K = \exp(\mu H_2 O^\circ - E_i) / kT (i = 1, 2)$$
(9)

From [5] and [6], we can find the relationship between  $P_{H_{2}O}$  and  $x_i$  (i = 1,2).

$$\ln P_{H_2O} = (E_1 - \mu H_2O^\circ)/kT + \ln x_1/(1 - x_1)$$
(10)

$$= (E_2 - \mu H_2 O^\circ)/kT + \ln x_2/(1 - x_2)$$
(11)

If  $E_2 - E_1 \approx 1$  eV and  $T = r.t. \sim 600$  K, water molecules begin to occupy site 2 after site 1 is almost occupied. These equations are none other than the Langmuir adsorption isotherm. It can be said that the above is the thermodynamic derivation of the Langmuir adsorption isotherm.

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Let us discuss the relationship by using the observed data from Fig. 6:

$$n = 0.187 (= a)$$
 at  $P_{1} = 4.45$  mmHg (12)

$$n = 0.206 (= b)$$
 at  $P_2 = 11.87$  mmHg (13)

If we assume  $x_1 \approx 1$  at these  $P_{H_2O}$ 's and  $\ln P_{H_2O}(\text{dry gas}) >> (E_1 - \mu H_2O^\circ)/kT$  (i.e.,  $E_1 - \mu H_2O^\circ <<-0.31 \text{ eV}$ ), the following can be derived:

$$N_1 = 0.154$$
 ( = *n* equilibrium with the dry gas) (14)

Transforming [11], we obtain

$$\ln P_{H_2 O} = (E_2 - \mu H_2 O^\circ) / kT + \ln n_2 / (N_2 - n_2)$$
(15)

Using  $P_1$ ,  $P_2$ , a, b, and  $N_1$  in [15], we obtain

$$\ln P_1 = (E_2 - \mu H_2 O^\circ)/kT + \ln(a - N_1)/(N_1 + N_2 - a)$$
(16)

$$\ln P_2 = (E_2 - \mu H_2 O^\circ)/kT + \ln (b - N_1)/(N_1 + N_2 - b)$$
(17)

Subtracting [17] from [16], we obtain

$$P_1/P_2 = (a - N_1)/(N_1 + N_2 - a) \cdot (N_1 + N_2 - b)/(b - N_1)$$
(18)

Substituting [12], [13], and [14] into [18], we obtain

$$4.45/11.87 = (0.187 - 0.154)/(0.154 + N_2 - 0.187) \cdot (0.154 + N_2 - 0.206)/(0.206 - 0.154)$$
(19)

Therefore,

$$N_2 = 0.079, \quad E_2 - \mu H_2 O^\circ = -0.125 \text{ eV}$$
 (20)

This result is consistent with the assumption expressed between Eq. 13 and Eq. 14. The  $x_2$  (occupancy of site 2) at  $P_1$  and  $P_2$  can be calculated from this result.

at 
$$P_1, x_2 = 0.42$$
 (21)

at 
$$P_2, x_2 = 0.66$$
 (22)

Let us examine whether these results agree with the observed data at intermediate  $P_{H_2O}$  in Fig. 6. From Fig. 6,

$$n = 0.199$$
 at  $P_{H_2O} = 7.75$  mmHg (23)

Thus,

$$\ln P_{H_2O} = -4.59 \tag{24}$$

$$(E_2 - \mu H_2 O^\circ)/kT + \ln n_2/(N_2 - n_1) = -4.55$$
(25)

The observed data are almost coincident with equation [15]. Similarly, the other observed data are also coincident with equation [15]. Since equation [15] is another expression of the Langmuir adsorption isotherm, this result indicates that the water adsorption into site 2 follows the Langmuir adsorption isotherm and the adsorption energy of site 2 is constant. In other words, it was demonstrated by thermodynamic discussion that water adsorption into site 2 follows the Langmuir adsorption isotherm. This result suggests that site 2 is located in a homogeneous plane-like interlayer because it has constant adsorption energy. More studies concerning the *n* vs.  $P_{H_2O}$  relationship (i.e., *n* vs.  $\mu H_2O$ ) are underway.

<u>Impedance Spectroscopy</u>. The changes of the K-HTB in complex impedance plot by water incorporation are shown in Figs. 7a-7f. The complex impedance plot of K-HTB with relative low water content is characterized by its positive values of Z'' (imaginary part of impedance), which can be explained by assuming a component of coil in the equivalent circuit of K-HTB.

It is not quite certain so far why the equivalent circuit apparently includes a component of coil. However, since samples with high electronic conductivity such as wire made of copper, plate of aluminum, etc., exhibit a complex impedance plot represented by an equivalent circuit including coil (as shown in Fig. 8), we can empirically conclude that this is the nature of samples with high electronic conductivity. The frequency dependence of the impedance (Z) of the equivalent circuit in Fig. 8 is represented by

$$Z = j\omega L + R_L \tag{26}$$

The complex impedance plot of the equivalent circuit in Fig. 8 is shown in Fig. 9. This is consistent with that of the water-free K-HTB immediately after reheating in Fig. 7a. This indicates that the water-free K-HTB has high electronic conductivity like metal and like the conventional K-HTB by a solid state reaction. On the other hand, the complex impedance plot after water incorporation is consistent with that of equivalent circuit in Fig. 10. Thus, we interpreted the profiles of the impedance diagrams by using the equivalent circuit in Fig. 10.

The frequency dependence of the impedance of the equivalent circuit in Fig. 10 is represented by

$$Z = j\omega L + R_L + R_C (1 - j\omega c R_C) / (1 + \omega^2 c^2 R_C^2)$$
(27)

 $R_L$  and  $R_C$  are estimated from Figs. 7a~7f and are plotted as a function of time in Fig. 11.  $R_C$  is dramatically increased from 6  $\Omega$  to 20000  $\Omega$ , whereas  $R_L$  remains almost constant (7  $\Omega$ ~30  $\Omega$ ). (The resistance of wire used for this measurement was 0.4  $\Omega$ . Thus it is negligible compared to  $R_L$ .) This indicates that a new component of high resistivity and high capacitance is generated in the circuit by incorporation of water and the new component hinders the conduction of electrons, whereas the part with high electronic conductivity remains unchanged. This suggests that the component of condenser ( $R_C$ , C) corresponds to interlayer or grain boundary of the sample pellet and that of coil ( $R_L$ , L) corresponds to grain. In other words, water molecules are incorporated in the interlayer or grain boundary and separate the path of electrons, which results in the increase of resistivity.



FIG. 7

The complex impedance plots of the K-HTB. The measurement was carried out using a sample pellet left in a humid atmosphere ( $P_{H_2O} = 11 \text{ mm Hg}$ ) for (a) 0 min, (b) 8 min, (c) 24 min, (d) 54 min, (e) 274 min, and (f) 1739 min.

The interfacial phenomena between the electrode and the sample pellet is negligible because the change of resistivity was observed by DC 4-probe measurement. The mechanism will be discussed in more detail later.



Z' / Ohm

FIG. 8 The equivalent circuit representing samples with high electronic conductivity.

FIG. 9 The complex impedance plot of the equivalent circuit in Fig. 8.

Structural Analysis. Slight changes in lattice parameters are observed by incorporation of water. The water-free K-HTB immediately after reheating has lattice parameters a = 7.3726 Å, c = 7.5570 Å (Fig. 12a); and the saturated K-HTB after 113 hours of water adsorption, a = 7.3868 Å, c = 7.5085 Å (Fig. 12c). Lattice parameter a is increased by ca. 0.01 Å, and lattice parameter c is decreased by ca. 0.05 Å. Moreover, superlattice structure every six layer along c axis emerged by incorporation of water as shown in Figs. 12b and 12c. After reheating the saturated sample in Fig. 12c, the XRD spectrum returned to that of the water-free one in Fig. 12a. In other words, these structural changes are reversible in response to adsorption and desorption of water molecules.

The mechanism of the resistivity-change in this connection is discussed as follows. Oxygen vacancies exist every six layers along c axis, as shown in Fig. 13. Water molecules are incorporated into these vacancies as coordinated water or structural water, and



FIG. 10 The equivalent circuit used for the interpretation of the impedance diagrams in Figs. 7a-7f.



FIG. 11

The changes of R<sub>C</sub> and R<sub>L</sub> in Fig. 10 by incorporation of water. R<sub>C</sub> and R<sub>L</sub> are estimated from Figs. 7a-7f.





(c)

### FIG. 12

The powder XRD profiles (a) immediately after reheating, (b) after 67 hours of water incorpora-tion in a humid atmosphere R.H. 100%; and (c) after 113 hours of water incorporation in a humid atmosphere R.H. 100%.



FIG. 13

The layer structure model suggested in this study. A rhombus corresponds to a  $WO_6$  octahedron.

structural changes (as shown in Fig. 13) take place. Because of these structural changes, the path of electrons along c axis is separated. This model is coincident with the result of the impedance spectroscopy discussed earlier in this paper. In this structural model, water molecules can be accommodated into vacancies up to  $H_2O/W = 0.167$ . Judging from this  $H_2O/W$  ratio, these oxygen vacancies corresponds to site 1 (see discussion on water vapor pressure/water content relationship). Site 2 is assumed to be located between water molecules in site 1 and terminal oxygen (W = O). It is unlikely that site 2 is located in the grain boundary because the n vs.  $P_{H_2O}$  relationship indicates that site 2 has constant adsorption energy. More studies are needed to provide more details.

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### REFERENCES

- 1. C.D. Chandler, C. Roger and M.J. Hampden-Smith, Chem. Rev. 93, 1205 (1993).
- 2. B. Gerand, G. Nowogrocki, J. Guenot and M. Figlarz, J. Solid State Chem. 29, 429 (1979).
- 3. M. Figlarz, Chemica Scripta 28, 3 (1988).
- 4. T. Kudo, A. Kishimoto, J. Oi and H. Inoue, Solid State Ionics 40/41, 567 (1990).
- 5. T. Kudo, J. Oi, A. Kishimoto and M. Hiratani, Mater. Res. Bull. 26, 779 (1991).
- 6. I. Tsuyumoto, A. Kishimoto and T. Kudo, Solid State Ionics 59, 211 (1993).
- 7. J. Oi, A. Kishimoto and T. Kudo, J. Solid State Chem. 103, 176 (1993).
- 8. M.F. Pye and P.G. Dickens, Mater. Res. Bull. 14, 1397 (1979).
- 9. I. Tsuyumoto, A. Kishimoto and T. Kudo, in *Solid State Ionic Materials*, eds. B.V.R. Chowdari, M. Yahaya, I.B. Talib and M.M. Salleh, p. 387, World Scientific, Singapore (1994).
- 10. I. Tsuyumoto and T. Kudo, Sensors and Actuators B (to be published).
- 11. T. Kudo, H. Okamoto, K. Matsumoto and Y. Sasaki, Inorg. Chim. Acta 111, L27 (1986).