

# Electrochemical Investigations of Polycrystalline $H_xNb_2O_5$

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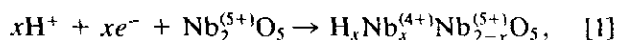
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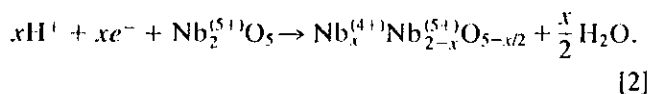
Polycrystalline samples of  $H_xNb_2O_5$  were prepared by electrochemical reduction of pressed and sintered powder samples of the H-Nb<sub>2</sub>O<sub>5</sub> modification. The hydrogen content of the bronze was determined by redox titration. The electrode potential showed that the bronze is thermodynamically unstable with respect to decomposition into Nb<sub>2</sub>O<sub>5</sub> and gaseous hydrogen. The hydrogen loss obeys a second-order rate law. The electrode potential fulfills Nernst's law with a square dependence on the hydrogen content. The specific resistance of H<sub>0.18</sub>Nb<sub>2</sub>O<sub>5</sub> determined by four-point dc measurements amounts to  $\rho(30^\circ\text{C}) = (0.0110 \pm 0.0015) \Omega \text{ cm}$ . The protonic conductivity of the bronze was substantiated by polarization experiments and the diffusion coefficient of H<sup>+</sup> ( $D \approx 5 \times 10^{-9} \text{ cm}^2/\text{sec}$ ) was estimated from the rate law of the depolarization voltage. © 1995 Academic Press, Inc.

## INTRODUCTION

Nb<sub>2</sub>O<sub>5</sub> is a promising material for electrochromic devices (1, 2). Investigations of thin Nb<sub>2</sub>O<sub>5</sub> films during and after the application of a cathodic current have been reported in several papers (3-6). The films were prepared by oxidation of Nb rods in air at 500-580°C (T-Nb<sub>2</sub>O<sub>5</sub>, designations of Nb<sub>2</sub>O<sub>5</sub> modifications according to (7)), of NbN<sub>x</sub> at 250-300°C (amorphous Nb<sub>2</sub>O<sub>5</sub>), or by anodic oxidation of Nb electrodes. By cathodic polarization a blue color and electric conductivity appear, which are typical properties of hydrogen bronzes. Besides



the formation of partially reduced Nb<sub>2</sub>O<sub>5</sub> has to be taken into consideration:



The product that is formed in a H<sub>2</sub>/H<sub>2</sub>O atmosphere at 1300°C (7), bleaches when kept at 650°C for 4 hr, but maintains its structure. Its structure is different from that

of H-Nb<sub>2</sub>O<sub>5</sub> (7, 8). However, the X-ray diffraction patterns of our pressed H-Nb<sub>2</sub>O<sub>5</sub> powder samples, recorded with a Siemens D500 diffractometer, show no significant differences before reduction and after bleaching. The observed reaction was found to change the bulk properties of the samples. This observation could be confirmed by *in situ* X-ray diffraction measurements (13). Thus it can be concluded that the reaction in question is reaction [1], because the oxygen cannot leave the Nb<sub>2</sub>O<sub>5</sub> bulk at room temperature as would be necessary for reaction [2].

From measurements of impedance (4), and of coulombic capacities during potentiodynamic cycling (9), as well as of optical examinations (6), it has been concluded that hydrogen enters Nb<sub>2</sub>O<sub>5</sub>. Contrary to other bronzes, e.g., H<sub>x</sub>MoO<sub>3</sub>, a special property of Nb<sub>2</sub>O<sub>5</sub> and H<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> is their insolubility in aqueous acid solutions. Therefore it was possible to carry out our electrochemical experiments in such media.

Our work on the electrochemical properties of reduced powder samples of H-Nb<sub>2</sub>O<sub>5</sub>, which also treats the bulk insertion of hydrogen, should be useful with regard to further applications.

## EXPERIMENTAL

### Preparation of Pressed Powder Samples and Hydrogen Content

The chemical reduction of Nb<sub>2</sub>O<sub>5</sub> powders (Alfa, 99.9%, X-ray diffraction shows a mixture of H-Nb<sub>2</sub>O<sub>5</sub> and M-Nb<sub>2</sub>O<sub>5</sub>) with Zn in aqueous solutions of HCl, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, or CH<sub>3</sub>COOH for some hours leads to a deeply blue coloration of the powder, which vanishes at room temperature when exposed to air. The same coloration is also obtained by electrochemical reduction of pressed Nb<sub>2</sub>O<sub>5</sub> powders. This method allows subsequent studies in an electrochemical cell continuously flushed with nitrogen at a constant temperature of 30°C (Fig. 1). Instead of using a fritted glass tube to separate the platinum counter electrode from the main cell, which leads to a large concentration gradient, the counter electrode was rinsed with nitrogen. Prior to the electrochemical investigations, the pressed powder samples (500 MPa, c.d. 13

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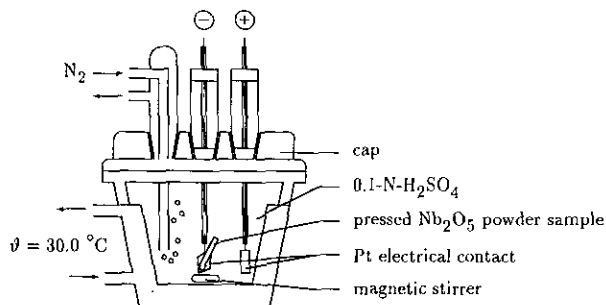
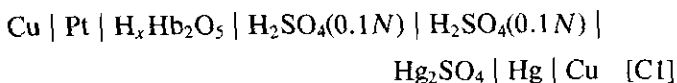


FIG. 1. Apparatus for the preparation and electrochemical investigation of niobium hydrogen bronze.

mm, thickness 1.5–2.5 mm, weight 0.5–1.0 g, density  $d = (2.6 \pm 0.1) \text{ g/cm}^3$ ) were heated in air to  $1200^\circ\text{C}$  for 5 hr in order to obtain pure  $H-Nb_2O_5$ , which was confirmed by X-ray diffraction (ASTM card index, 37-1468) (7, 10). The tablets were wedged in a suitably formed platinum sheet which simultaneously served as the electrical contact. After applying a constant cathodic current of 1.00 mA for 10 hr, whereby also some hydrogen gas was formed, the hydrogen content  $x$  as well as the electrochemical potential in aqueous  $H_2SO_4$  and the resistance of the samples reached constant values which were assumed to correspond to complete reduction at 1 bar  $H_2$  pressure. Determinations of  $x$  immediately after the electrochemical reduction of the samples led to values up to 0.25. This may be explained by hydrogen adsorption at the surface of the bronze. However, when the tablets were left in the cell for 10–20 min after switching off the current, the results were reproducible. The value of  $x = 0.180 \pm 0.006$ , which was then determined by iodometric titration, agrees well with 0.2 found by coulometric charging of thin amorphous  $Nb_2O_5$  films (3). The highest hydrogen content published for  $T-Nb_2O_5$  also amounts to  $x = 0.2$  (5). Experiments with a mixture of  $M-Nb_2O_5$  and  $H-Nb_2O_5$  (identified by X-ray diffraction after heating to  $1000^\circ\text{C}$  for 4 hr) showed no significant differences in  $x$  compared with the pure H phase. Thus, the stoichiometry of  $Nb_2O_5$  reduced at 1 bar hydrogen partial pressure seems to be largely independent of the modification type.

#### Potential Measurements

Measurements of the electrochemical potential of  $H_xNb_2O_5$ , which gave information about the thermodynamic properties and the stability of the bronze, were performed in an apparatus (Fig. 1) equipped with a  $Hg|Hg_2SO_4|H_2SO_4(0.1N)$  reference electrode, which was separated by a frit from the main cell. The electrode potential  $E(H_xNb_2O_5)$  of cell [C1]



$$E(H_xNb_2O_5) = E(Hg | Hg_2SO_4 | H_2SO_4(0.1N)) - \Delta E(C1) \quad [3]$$

( $E(Hg | Hg_2SO_4 | H_2SO_4(0.1N)) = 679.4 \text{ mV}$  (11, 12),  $\vartheta = 30^\circ\text{C}$ , and  $a(H_2SO_4) = 1.748 \times 10^{-5} \text{ mole}^3/\text{liter}^3$ ), increased with time after switching off the cathodic current (Fig. 2a)). The potential of a completely reduced  $Nb_2O_5$  sample is  $-0.42 \text{ V}$  vs NHE. Consequently,  $H_xHb_2O_5$  is thermodynamically unstable at  $30^\circ\text{C}$  in the presence of a 1 bar hydrogen partial pressure. But the order of magnitude of the decomposition pressure  $P_d$  (Eq. [6]) shows that the decomposition of the bronze is inhibited by a large kinetic hindrance.

The  $E(H_xNb_2O_5)$  vs  $t$  curve (Fig. 2a) could be fitted by Eq. [4] (Fig. 2b):

$$E(H_xNb_2O_5)(t) = \frac{2RT}{F} \ln \left( 6.57 \times 10^{-3} \frac{1}{\text{min}} t + \frac{1 \text{ mole}}{c_0 \text{ liter}} \right) - 0.404 \text{ V} \quad [4]$$

( $c_0 = 1.76 \text{ mole/liter}$ : concentration of  $H^+$  at  $t = 0$ ). Curve (c) of Fig. 2 which was measured during the application of an anodic current of 0.01 mA increases everywhere faster than that without current (curve b), indicating a supplementary decomposition. It was found that the differences  $\Delta E'$  between the values of  $E(H_xNb_2O_5)$  in the plots (b) and (c) were proportional to time, with  $s = 0.0150 \text{ mV/min}$  as the factor.

#### Interpretation of the Decomposition Kinetics and the Nernst Equation of the Bronze

As Eq. [4] is of the Nernstian type, with  $2RT/F$  as the prelogarithmic factor, its time function hides the kinetic

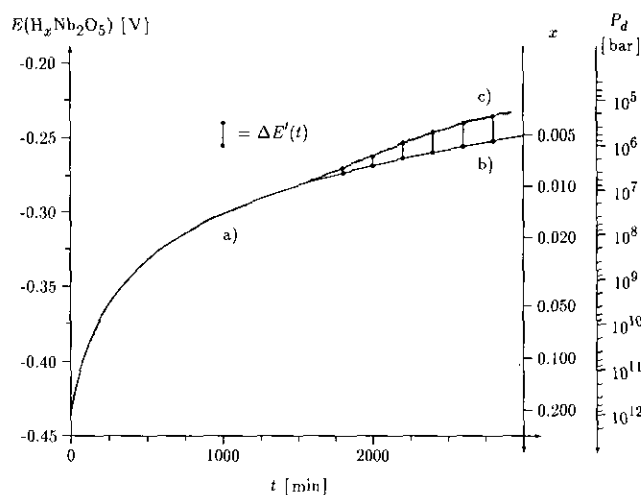
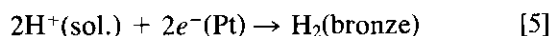


FIG. 2. (a) Potential of a  $H_xNb_2O_5$  sample (0.65 g  $Nb_2O_5$ ) vs time; cathodic charging stopped at  $t = 0$ . (b) Extrapolation of curve (a) by the fit function Eq. [4]. (c) Increase of  $E(H_xNb_2O_5)$  during an anodic current of 0.01 mA.

law of the hydrogen loss of the bronze. There are different ways besides Eq. [1] to formulate the electrode reaction of the bronze. When the bronze is regarded as a hydrogen electrode, a formal  $H_2$  pressure  $P_d(x)$  corresponds to the hydrogen content according to

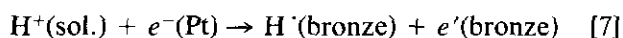


and

$$E = \frac{RT}{2F} \ln \left( \frac{a^2(H^+)}{P_d} \right) \quad [6]$$

( $a(H^+) = \text{constant proton activity in the solution}$ ).

The order of magnitude of these pressures  $P_d$  calculated from Eq. [6] (cf. Fig. 2) shows, that the formation of hydrogen gas is thermodynamically strongly favored. Nevertheless, this reaction is slow and apparently determined in its kinetic law by the special form of hydrogen within the bronze. This becomes obvious, when the electrode reaction is written in an unusual manner



with

$$E = E^0 + \frac{RT}{F} \ln \left( \frac{a(H^+)}{a(H')a(e')} \right), \quad [8]$$

where  $H'$  and  $e'$  are Kröger-Vink symbols. When the activities,  $a(H')$  and  $a(e')$ , are replaced by concentrations,  $c(H')$  and  $c(e')$ , and are set equal, Eq. [8] may be written in a form which is comparable with Eq. [4]:

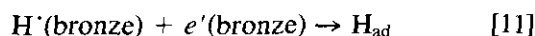
$$E = E^0 + \frac{2RT}{F} \ln \left( \frac{\sqrt{a(H^+)}}{c(H')} \right), \quad [9]$$

By this comparison it is now clear, that  $c(H')$  decreases during the decomposition of the bronze according to a second-order reaction law

$$\frac{1}{c(H')} = \frac{1}{c(H')_m} + kt, \quad [10]$$

where  $c(H')_m$  is the maximal concentration of  $H'$  and  $k$  is a reaction constant (values discussed elsewhere (13)).

It can be concluded that the reaction in question is probably



rather than the Tafel reaction between two hydrogen adsorbed atoms ( $H_{ad}$ ), because the anodic experiment

(curve (c) in Fig. 2) gave a further argument for Eqs. [8] and [9] as the correct Nernst equation of the bronze electrode: Constant rate oxidation of hydrogen by a small current must lead to a linearly falling concentration  $c(H')(t) = c(H')(t=0) - \alpha t$ , where  $\alpha$  is given by Faraday's law. As the concentration changed only slowly, its variation in Eq. [9] can be expressed by a series expansion

$$\Delta E = \frac{2RT}{F} \frac{\alpha}{c(H')(t=0)} t = st \quad [12]$$

which led to the experimentally found value  $s \approx 0.015$  mV/min.

### Specific Resistance

The resistivities  $\rho$  of  $H_x\text{Nb}_2\text{O}_5$  powder samples were measured by the four-point as well as by the two-point method. Silver wires attached to the tablet with silver conducting paste were used for electrical leads (Fig. 3). After the electrochemical reduction, the aqueous  $H_2SO_4$  was removed from the cell applying a small  $N_2$  overpressure. Then the whole cell was thoroughly washed with distilled oxygen-free water. The dc measurements were carried out while the sample was suspended in this water. The temperature of the sample could be kept constant in this way. It was observed that the decomposition rate of the bronze is lower in  $N_2$ -saturated water than in purified gaseous  $N_2$ .

The results of the four-point measurements may be summarized as follows:

- In the investigated range from 0 to 1.5 mA the  $U-I$  characteristics follow Ohm's law.
- During the first 10 hr of the electrochemical reduction the hydrogen content  $x$  increases and the resistivity falls to  $\rho = (0.0110 \pm 0.0015) \Omega \text{ cm}$  (30°C). Further reduction will not decrease this value.

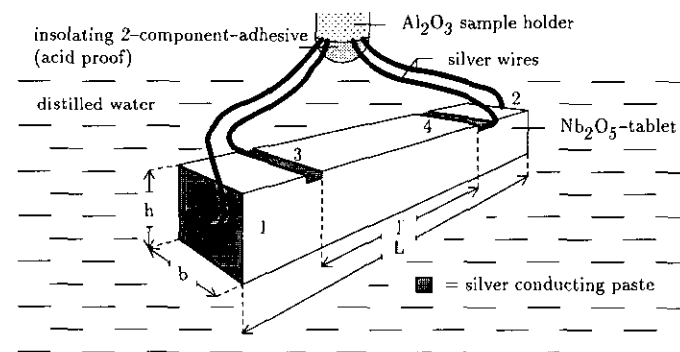


FIG. 3.  $Nb_2O_5$  tablet with contacts (1, 2 = current contacts; 3, 4 = voltage contacts).

• The resistivity does not depend on the geometry of the sample which indicates the intercalation of hydrogen to be a volume effect. This presumption was proved by *in situ* X-ray diffraction measurements (13).

• The temperature dependence of  $\rho$  has been determined qualitatively.  $\rho$  decreases with temperature, which is typical for semiconductors.

• During the decomposition of the bronze in  $N_2$ -saturated water as well as in air, the  $\rho$  vs  $t$  curves increase monotonically in the range  $0.01 < \rho < 50 \Omega \text{ cm}$ .

The purity of the water was checked before and after each measurement: After removing the sample the resistance between the silver wires in the water always exceeded 100 k $\Omega$ .

The  $U$ - $I$  characteristics of the two-point measurements show a hysteresis, caused by ionic polarization (see below). Here, measured values of  $\rho$  which depend mainly on the contact resistances  $R_C (= R_{C1} + R_{C2} \approx 50 \Omega)$ , are more than 200 times larger than those determined by the four-point method.

The electronic impedance of  $H_xNb_2O_5$  samples can be described by a  $RC$  network, consisting of the contact resistances and the contact capacities in series with the ohmic resistance  $R_T$  of the tablet determined by the four-point measurements (Fig. 4b).

### Polarization Experiments

A dc voltage between the contacts of the  $H_xNb_2O_5$  sample induces a concentration gradient of the  $H^+$  particles (Fig. 4a). After switching off the current, the depolarization voltage between the contacts was measured (Fig. 5). With the help of two-point ac measurements at

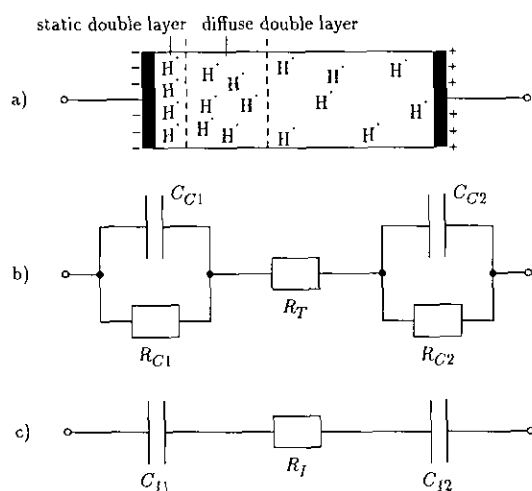


FIG. 4. (a) Schematic representation of the hydrogen gradient in a polarized  $H_xNb_2O_5$  sample. The equivalent-circuit diagrams for the electronic (b) and ionic (c) conductivity.

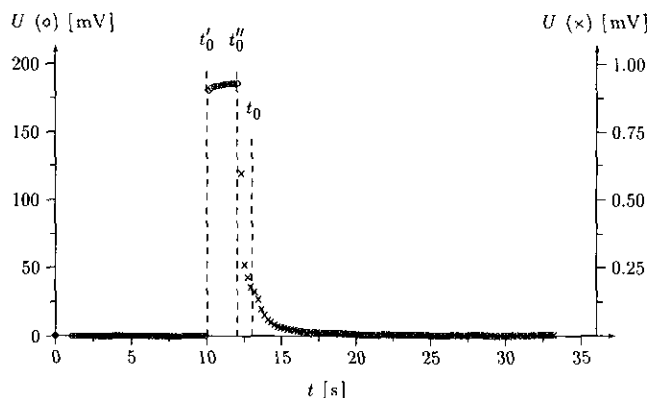


FIG. 5. Depolarization experiment:  $t_0' \leq t \leq t_0''$ , polarization process;  $t_0'$ , time of cutting off the current;  $t_0$ , point of inflection. The left scale is for  $t < t_0'$ , the right scale is for  $t > t_0''$ .

three frequencies, the time constant  $R_C C_C$  was estimated as 50  $\mu\text{sec}$ . Thus, the decrease in the voltage observed in the depolarization experiments, which had a time resolution of 0.2 sec, cannot be caused by an electronic effect. All curves show a point of inflection at  $t_0 \approx t_0'' + 1$  sec, with  $t_0$  largely independent of the polarization time  $t_p = t_0'' - t_0'$ . Therefore, two processes seem to take place, while the ionic capacitors  $C_{11}$  and  $C_{12}$  shown in Fig. 4c discharge. The first process prevailing for  $t_0' < t < t_0$  seems to be the decomposition of the diffuse double layer of  $H^+$  ions and the second for  $t > t_0$  probably represents a diffusion-controlled decomposition of the static double layer at the contact surface between the tablet and the negative pole. Using the solution of Fick's second law valid for the momentaneous diffusion source

$$c(x, t) = \frac{n}{F\sqrt{\pi D}(t - t_0)} e^{-x^2/4D(t - t_0)}, \quad [13]$$

( $0 \leq x \leq L$ ;  $n = V_0(c_S(t_0) - c_0)$ ; where  $F = bh$  is the area of section of the tablet;  $D$  is the diffusion coefficient of  $H^+$ ;  $V_0$  is the volume of the static double layer,  $c_S(t_0)$  and  $c_0$  are the concentrations of  $H^+$  inside and outside of the static double layer at  $t = t_0$ , respectively, and the proportionality  $I = U/R \propto \partial c(x = 0, t)/\partial t$ , it is possible to explain the depolarization curves by a  $H^+$  diffusion starting at  $t = t_0$  (12). Hence,

$$U = -Re_0 N_A d_0 \frac{n}{2\sqrt{\pi D}} (t - t_0)^{-3/2}. \quad [14]$$

Plots of  $U$  vs  $(t - t_0)^{-3/2}$  (Fig. 6) demonstrate the validity of Eq. [14]. The slopes of the straight lines increase with  $t_p$  according to growing  $c_S(t_0)$  and  $V_0$  values.

With respect to the Nernst-Einstein relation and the estimations  $c_S(t_0) = 55$  mole/liter and  $V_0 = 1 \text{ \AA} \cdot F$  (12), it

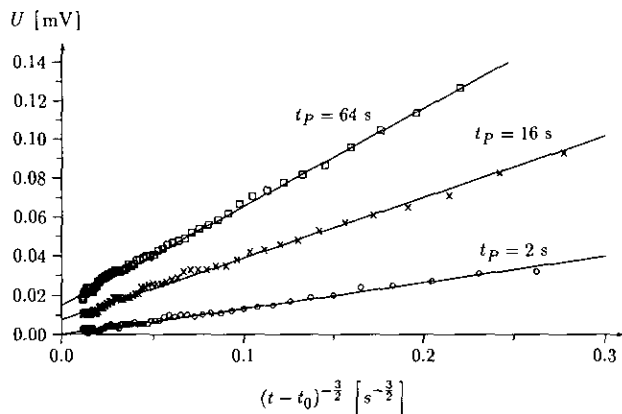


FIG. 6. Plots of three depolarization experiments.

is possible to determine the magnitude of the diffusion coefficient  $D$  of  $H^+$  in the  $H_xNb_2O_5$  samples: The calculated values between  $10^{-9}$  and  $10^{-8}$   $cm^2/sec$  are in good agreement with those found for thin films of  $H_xNb_2O_5$  (1, 3).

### CONCLUSION

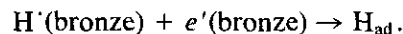
The main results of this study can be summarized as follows:

- The bronze  $H_xNb_2O_5$  ( $x_{max} = 0.18$ ) is a semiconductor ( $\rho_{min} = 0.011 \Omega cm$ ).
- Protonic conductivity is revealed by depolarization experiments. The depolarization voltage fulfills a  $t^{-3/2}$  rate law, indicating the decomposition of a rigid  $H^+$  double layer (diffusion coefficient between  $10^{-9}$  and  $10^{-8}$   $cm^2/sec$ ).
- The Nernstian equation of the bronze electrode can

be formulated considering the intercalated electrons ( $e'$ ) to be an individual chemical component:



- The bronze is thermodynamically unstable with respect to a hydrogen gas evolution. The determinative step of the decomposition reaction which follows a second-order rate law is probably



### ACKNOWLEDGMENT

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