Proton conductivity of layered niobium-doped tungsten oxide hydrate system at intermediate temperature

Yumi Tanaka, Hiroaki Matsuda, Mitsuhiro Hibino and Tetsuichi Kudo

Institute of Industrial Science, University of Tokyo
7-22-1 Roppongi, Minato-ku, Tokyo, 106-8558 Japan
Fax: 81-03-3402-6350, e-mail: yumi@iis.u-tokyo.ac.jp

A series of niobium-doped tungsten trioxide dihydrates was synthesized and their proton conductivities were investigated. XRD measurements indicated that all samples maintained the primary layered structure of $WO_3 \cdot 2H_2O$ in which a hydrogen bond network extended. A liner change in lattice parameters with the Nb doping level was observed below $Nb/(W+Nb)=0.062$. In the intermediate temperature range (323-423K), conductivity of all samples stayed almost constant above the water vapor pressure where dehydration from dihydrate to monohydrate occurred. This indicates that the proton conduction occurred mainly not on the surface but in the bulk utilizing a hydrogen network at higher relative humidity. Conductivity increased with increasing in Nb content in the range of $0 \leqq Nb/(W+Nb) \leqq 0.062$. This is probably because protons as a charge carrier are generated as a result of charge compensation.

Key words: Tungsten oxide hydrate, proton conductor, fuel cell, hydrogen bonding network

1. INTRODUCTION

Solid state proton conductors are divided into two types by temperature where they work as a solid electrolyte. Perovskite-type oxides such as $Sr(Ce,Yb)O_3$ or $Ba(Ce,Nd)O_3$, representing the high temperature type, show high conductivity ($\sigma = 0.01Scm^{-1}$) in the region above 600 ℃ [1-2]. It is believed that proton is transferred between framework oxygens by a hopping mechanism assisted by extended oxygen vibration. On the other hand, the low or room temperature type is represented by organic polymer proton conductors like perfluorosulphonic membrane (Nafion) practically used for Polymer Electrolyte Fuel Cells (PEFC) and inorganic polyacids such as $H_3[PW_{12}O_{40}]nH_2O$ [3]. It is also known that some metal oxide hydrates like $ZrO_2 \cdot nH_2O$ and $SnO_2 \cdot nH_2O$ exhibit considerable conductivity around room temperature [4] mainly due to proton migration through surface absorbed water. However, conductivity of those inorganic compounds falls rapidly with release of water, if they are heated to temperature like 100 ℃. The situation is similar for polymer membrane electrolytes. To date, no proton conductive solid electrolyte applicable to the 100-500℃ range has been developed, though such an intermediate temperature range is advantageous to fuel cells especially for vehicle propulsion. For fuel cells fed with reformed gas, higher temperature operation is needed to protect platinum-based catalysts from the poisoning by carbon monoxide inevitably contained in fuels. Moreover, the total system efficiency would be improved because the waste heat from fuel cell units could be easily recovered at higher temperature and re-used as heat needed at the reformer section. Thus, development of proton conductors for intermediate temperature range is strongly needed.

In most metal oxide hydrates, proton is transported by the surface mechanism through absorbed water, which departs easily at elevated temperature or low humidity.

However, as pointed out by Barboux et al. [5], there are a few compounds in this class in which proton migrates through crystalline water molecules (bulk mechanism). If the bulk mechanism is the case, conductivity of the compound may stay high in a relatively wide water vapor pressure, until crystalline water starts departing at considerably high temperature. Such a consideration prompted us to evaluate proton conductivity of some hydrate compounds at intermediate temperature under humidity conditions like those in fuel cells. We have already reported that tungsten oxide dihydrate ($WO_3 \cdot 2H_2O$), a layered compounds (Fig.1) having a hydrogen bonding network in its interlayer space (Fig.2), shows proton conductivity of about $0.01Scm^{-1}$ at 150℃ by a bulk mechanism [6]. High conductivity is maintained till the dihydrate turns to monohydrate at a low humidity level. The purpose of this study is to improve conductivity and stability of $WO_3 \cdot 2H_2O$ by doping it an alliovalent metal element. Here we report synthesis of a series of niobium-doped tungsten oxide dihydrates and

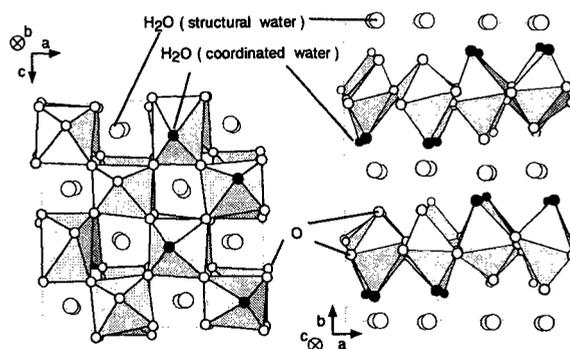Fig.1 Structure of $WO_3 \cdot 2H_2O$ projected onto the a-c plane (left) and the a-b plane (right).

⊗ : O of Interlayer water   ◯ : O double-bonding to Mo

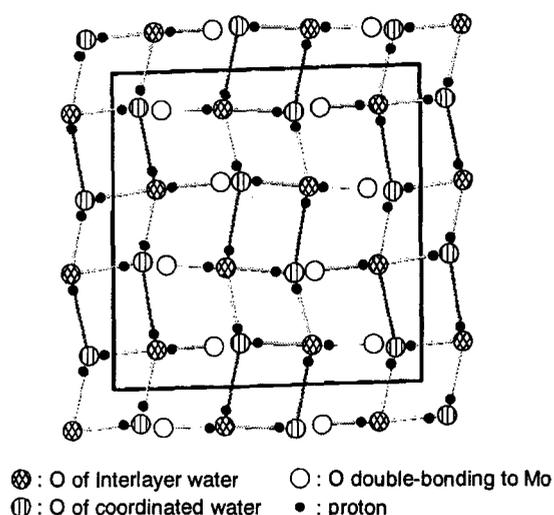⦶ : O of coordinated water   ● : proton

Fig.2 Schematic view of the network of hydrogen bond constructed by interlayer water, coordinated water and double-bonding oxygen.

their conductivity in the intermediate temperature range under high water vapor pressure.

2. EXPERIMENTAL

2.1 Materials preparation and characterization

Non-doped $WO_3 \cdot 2H_2O$ was synthesized according to Freedman [7]. In short a solution of Na_2WO_4 was hydrolyzed with HCl to precipitate a dihydrate sample. Niobium-doped samples were synthesized using a new technique as follows. Powder of metallic tungsten and niobium were separately dissolved in a hydrogen peroxide aqueous solution at room temperature and 80°C, respectively, to yield pale yellow peroxo-polytungstate and peroxo-polyniobate solutions. Excess H_2O_2 in each solution was removed catalytically with a platinized Pt net. The contents of tungsten and niobium were determined by ICP measurements. Those two solutions were mixed at an appropriate volume ratio, and a 5N NaOH solution was added. The mixed solution was kept stirred until it turned colorless with decomposition of peroxo-metallates. Then a 6N HCl was added to the solution thus obtained. A pale yellow precipitate appeared immediately, and it turned deep yellow in several hours. The yellow precipitate was filtrated, washed several times with pure water and dries in a desiccator.

The XRD patterns were recorded at room temperature on a Rigaku Rint 2100 diffractiometer system using CuKα radiation. Thermal analysis was performed on a Mac-Science 200S TG/DTA system and infrared spectra were recorded on a Shimazu FTIR-8100 using KBr pellets in which the samples were dispersed.

2.2 Proton conductivity measurement

Proton conductivity measurement was carried out under hydrothermal condition by the a.c. method using an impedance analyzer. Powdered samples were pressed to pellets (4mm in diameter, 1-3mm in thickness and 60-80% of theoretical density). At the same time,
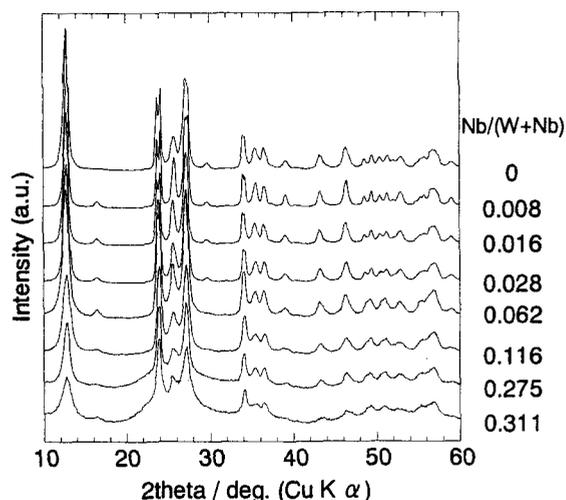

Fig.3 XRD patterns of a series of Nb-doped samples; $0 \leqq Nb/(W+Nb) \leqq 0.311$

acetylene black was attached on both sides of pellets as electrodes. Hydrothermal condition up to 150°C was made within a stainless pressure-resistant vessel. Water pressure was controlled by a leak valve.

3. RESULTS AND DISCUTTION

3.1 Materials characterization

Powder XRD patterns recorded with samples in the system of niobium-doped tungsten oxide dihydrates are shown in Fig.3. Each profile is basically the same as that of non-doped $WO_3 \cdot 2H_2O$ (Nb/(W+Nb)=0), which takes a layered structure as shown in Fig.1 : Each tungsten atom is surrounded by one terminal oxygen, one coordinated water and four bridging oxygens with which $WO_5(H_2O)$ octahedra are connected with each other to form a neutral $WO_3 \cdot H_2O$ layer : The other half of water molecule, not bonded to tungsten, sits between such layers as interlayer crystal water : Since the distance
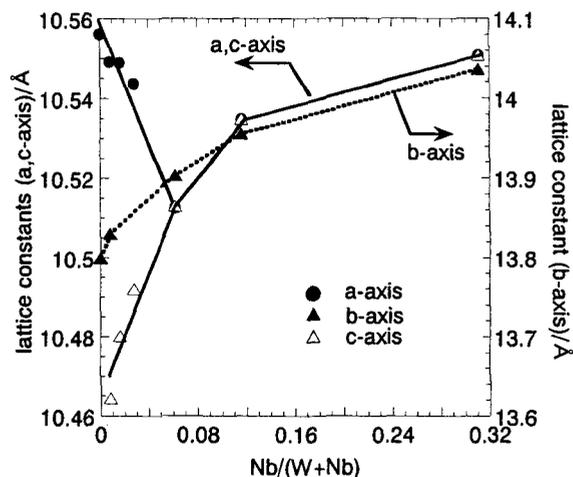

Fig.4 Lattice constants (a,b and c-axis) of a series of Nb-doped samples; $0 \leqq Nb/(W+Nb)$ as a function of $Nb/(W+Nb) \leqq 0.311$

between oxygens of those two kinds of water is relatively short (2.6-3.1A), it is believed that a hydrogen bonding network extends along the layers. Fig.3 confirms that doped niobium successfully replaces tungsten atoms in such a structure. We have not succeeded in preparing samples with a higher dopant level, because of a side reaction in the synthetic procedure.

The lattice parameters of the compounds are changed with doping niobium, as shown in Fig.4. The a-axis is shortened linearly up to the doping level of Nb/(W+Nb)=0.062, while the c-axis shows a linear elongation. The b-axis ($\perp$ layer) is also prolonged almost linearly, though the change is relatively small. The compound becomes tetragonal (a=c) at Nb/(W+Nb) =0.062. After passing a (quasi-)orthorhombic (β =91.04 for $WO_3 \cdot 2H_2O$) to tetragonal transition, both parameters shows a gradual increase to Nb/(W+Nb)=0.311.

Fig.5 shows infrared spectra recorded for samples with various doping levels. The bands in the range from 3000 to $3600cm^{-1}$ are due to the OH stretching vibrations. In the case of non-doped $WO_3 \cdot 2H_2O$ (Nb/(W+Nb)=0), at least four peaks can be resolved in this range, reflecting the existence of two kinds of water molecule and three kinds of OH bond with different distances. According to Krebs [8], isostructural $MoO_3 \cdot 2H_2O$ shows a similar OH band split. The present doped samples also show a similar split, if its niobium content is low. However, the peak splitting becomes unclear, as the doping level is more increased. This suggests that the arrangement of water molecules becomes disordered with doping niobium. It is also likely that vacancies of coordination water by doping. A (quasi-)orthorhombic to tetragonal transition observed by XRD can be explained assuming such a situation.

Results of the thermal analysis also indicate that niobium doping reduces individual characters of two kinds of water. As shown in Fig.6, a non-doped sample shows a clear two-step weight loss on heating. The first one is due to departure of interlayer water, and the
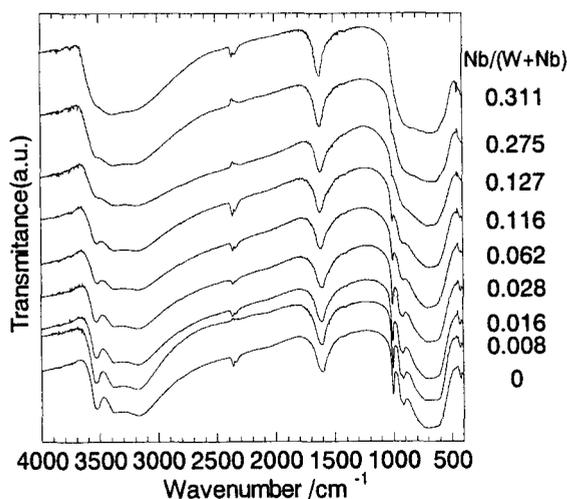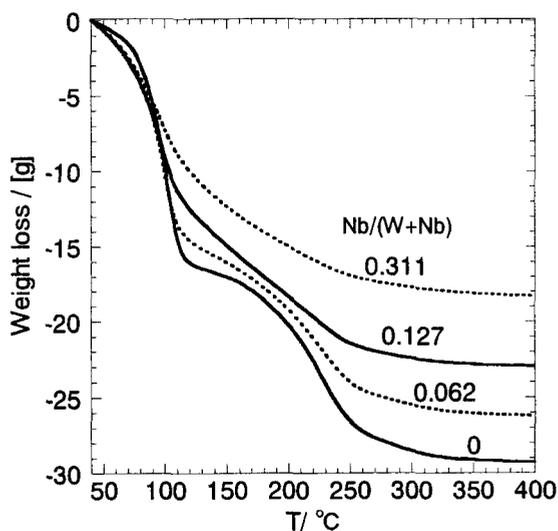

Fig.6 TG curves for a series of Nb-doped samples; $0 \leq$ Nb/(W+Nb)≤ 0.311. The weight loss is provided per one mole of metals.

second coordination water. However, the step becomes vaguer and disappears with increasing the niobium content.

In Fig.6, we can also notice that the total water content of each sample is decreased with increasing niobium. If charge deficiency generated by doped Nb^{5+} is compensated with proton, doped compounds may be expressed formally as:

$$H_xW_{1-x}Nb_xO_3 \cdot nH_2O \qquad [I]$$
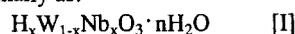
The values of n calculated on this scheme using observed weight loss data (Fig.6) are plotted against the Nb content in Fig.7, showing substantially n=2-x. (Note that each final product at 350°C (in Fig.6) is assumed as $H_xW_{1-x}Nb_xO_3$ or $W_{1-x}Nb_xO_{3-x}(OH)_x$). Proton introduce
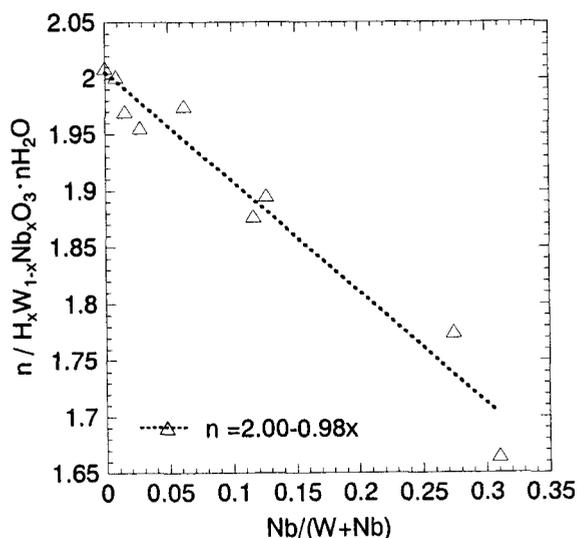

Fig.5 IR profiles of a series of Nb-doped samples; $0 \leq$ Nb/(W+Nb)≤ 0.311

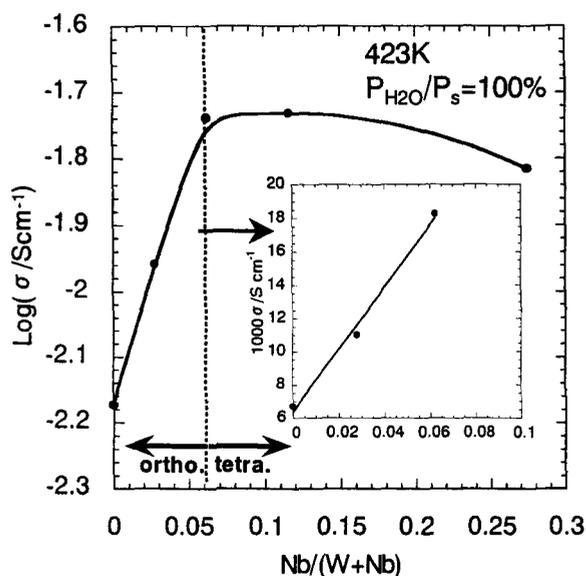Fig.7 Water contents n in $H_xW_{1-x}Nb_xO_3 \cdot nH_2O$; $0 \leq$ Nb/(W+Nb) ≤ 0.311 as a function of Nb/(W+Nb) determined by TG.
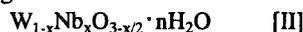
Fig.8 Proton conductivity of a series of Nb-doped samples; $0 \leq$ Nb/(W+Nb) ≤ 0.311 at 423K as a function of Nb/(W+Nb)

by Nb-doping seems to move in the interlayer space, because no signal due to W-OH or Nb-OH is observed by the infrared spectrum. This is a situation that we expected for niobium doping. However, another scheme assuming oxygen vacancies

$$W_{1-x}Nb_xO_{3-x/2} \cdot nH_2O \qquad [II]$$

cannot be abandoned, because the same n-x relationship is also expected for this case.

3. 2. Proton conductivity

We have already reported [6] that, in the range of 100-150 °C , the conductivity(σ) vs. water vapor pressure (p) isotherm of non-doped $WO_3 \cdot 2H_2O$ has a relatively wide σ -plateau extending to the saturated pressure (p_s) at the relevant temperature, or its conductivity stays at a high level until water vapor pressure is lowered to a certain value at which the compounds start decomposing. Every present doped sample showed a similar behavior. A plateau in the σ -p isotherm is characteristic of the bulk mechanism. It is, therefore, thought that proton in the present compounds is not transported by the surface mechanism through absorbed water but by the bulk mechanism utilizing a hydrogen bond network between the layers.

Fig.8 shows plots of conductivity vs. doped Nb content at 150°C under saturated water vapor pressure ($p/p_s=1$). Conductivity increases with increasing Nb almost linearly (as shown in the superimposition) in the doping range of x=0-0.062, coinciding to the (quasi-)orthorhombic region. Compound at x=0.062 shows conductivity of about $0.02Scm^{-1}$, which is four times larger than that of the mother dihydrate. This is probably because proton as a charge carrier is increased by doping according to scheme [I]. In the more doped tetragonal region, however, conductivity levels off or rather tends to decrease. It is reasonable to assume that the doping scheme is changed from scheme [I] to [II], as

the Nb content is increased. The latter scheme does not generate excess proton. Moreover, it decreases water molecules needed to form the hydrogen bonding network. Somewhat lower conductivity at x=0.275 might be caused by such an effect.

4. CONCLUSION

To enhance proton conductivity of tungsten oxide dihydrate, doping of niobium into this mother compound was attempted. Doped compounds were successfully obtained in the doping range of $0 \leq x=Nb/(W+Nb) \leq 0.311$ by our original synthetic route using peroxo-polyacids of W and Nb as a starting material.

The structure was (quasi-)orthorhombic in the region of x<0.062, while tetragonal x>0.062. It was found that conductivity increased with increasing Nb up to x=0.062, and reached about $0.02Scm^{-1}$ at 150 °C in humid conditions. Such an increase in conductivity is probably due to excess proton generated as a result of niobium doping. A composite of doped $WO_3 \cdot 2H_2O$ and a heat resistive polymer as a proton conductor membrane is being developed.

6.REFERENCES
[1] H.Iwahara, T.Esaka, H.Uchida, H.Maeda, Solid State Ionics 3/4 (1981) 359
[2] H.Iwahara, T.Shimura, H.Matsumoto, Electrochemistry 68 (2000) 154
[3] O.Nakamura, T.Kodama, I.Ogino, Y. Miyake, Chem. Lett. (1979) 17
[4] W.A.England, M.G.Cross, A.Hanmett, P.J.Wiseman, J.B.Goodenough, Solid State Ionics 1 (1980) 231
[5] P.Barboux, R.Morineau, J.Uvage, Solid State Ionics 27 (1988) 221
[6] Y.M.Li, M.Hibino, M.Miyayama, T.Kudo, Solid State Ionics 134 (2000) 271
[7] M.L.Freedman, J. Am. Chem. Soc. 81 (1959) 3834
[8] V.B.Krebs Acta Cryst. B28 (1972) 2222