（様式３）

博士論文の要約

氏　　名　内村　祐

論文題目　Study on Materials Processing for Barium Titanium Oxyhydride with Hydride Ion and Electron Mixed Conductivity

A perovskite-type oxyhydride $BaTiO_{3-x}H_x$ is a unique compound exhibiting hydride ion and electron (H^-/e^-) mixed conductivity[1], anion exchangeability[2], and catalytic activity for NH_3 synthesis[3] and CO_2 methanation[4]. These conducting and catalytic natures should be promising for the use of hydrogen-permeable electrodes in electrochemical devices for chemical/energy conversion. However, the conventional synthesis method of ion exchanging using CaH_2 as a reducing agent[1] is easily affected by kinetic factors related to ion diffusion, such as the particle size of precursor oxide, making it difficult to control the H^- content x that is the critical matter for the above-mentioned chemical functions. Moreover, it also requires multi-step processes such as long sintering and washing of byproducts. Such a complexity of the synthesis method might result in poor reproducibility of functional performances and be unsuitable for future applications. The performance of $BaTiO_{3-x}H_x$ as an electrode material has not been verified. In this thesis, processing routes in the manner of powder and thin film of $BaTiO_{3-x}H_x$ were explored, and examined properties as hydrogen-permeable electrodes.

Firstly, $BaTiO_{3-x}H_x$ powder was directly synthesized by the mechanochemical method and functioned as the electrode for hydride ion conductors[5]. Starting materials of BaH_2, BaO, TiO_2, and TiH_2 were mixed with the nominal composition of $0 < x \leq 2$. The mixtures were dry-milled for 90 minutes in a ZrO_2 container with ZrO_2 balls filled with Ar gas at room temperature. The obtained powder was characterized by X-ray diffraction, neutron diffraction, thermal desorption spectroscopy, and thermogravimetry measurement, indicating that the target compound of $BaTiO_{3-x}H_x$ was successfully synthesized at $0 < x \leq 1$ (Figure 1). This compositional range is wider than that ($0 \leq x \leq 0.6$) of the conventional method using CaH_2 reduction, confirming the suitability of the mechanochemical method. The evaluation of electric conductivity at $x = 1$ showed that electronic conductivity was dominant under 100 ºC, whereas hydride ionic conductivity was dominant over 100 ºC. From the evaluation of both electric conductivity and thermogravimetry measurement, the desorption of hydride ion of the $BaTiO_{3-x}H_x$ ($x > 0.75$) was composed of two steps (~100 ºC and ~400ºC), although there is an only one-step (~400 ºC) desorption in $x < 0.60$. This result indicated that the materials which were mechanochemically synthesized through dry milling without heating showed different properties from the synthesis method with heating. Electrochemical cell composed of hydride ion conductor $LaSrLiH_2O_2$ powder sandwiched by $BaTiO_{3-x}H_x$ ($x = 0.5$) powder was evaluated by electrochemical impedance spectroscopy under H_2 atmosphere. This electrochemical experience indicated that $BaTiO_{3-x}H_x$ acted as a hydrogen-reversible electrode (Figure 2).

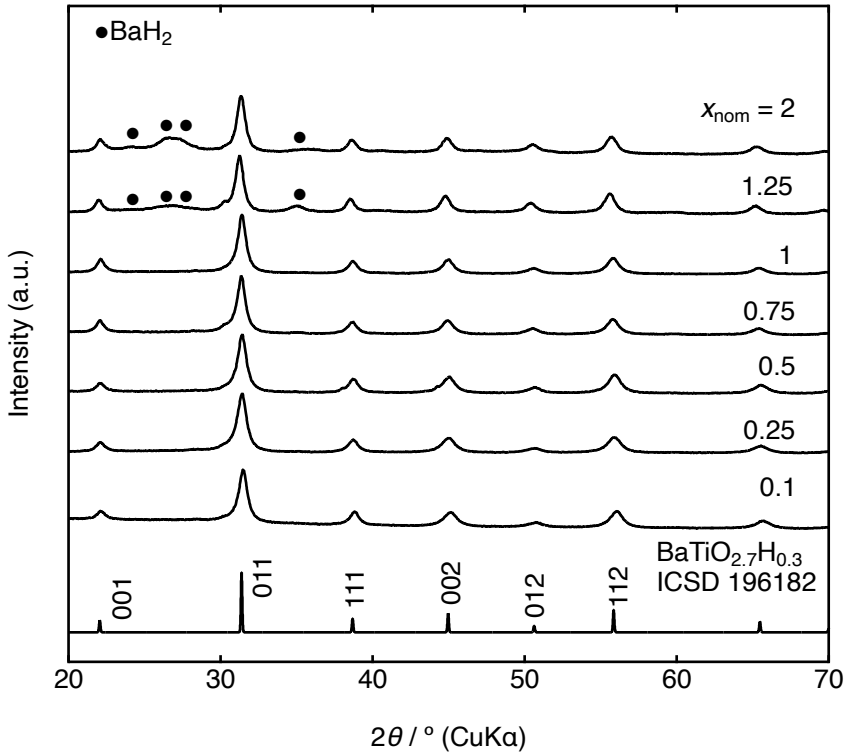

Figure 1 (a) Laboratory XRD patterns of $BaTiO_{3-x}H_x$ (x_{nom} = 0.1, 0.25, 0.5, 0.75, 1, 1.25, 2). Black circles in x_{nom} = 1.25, 2 indicate peaks derived from BaH_2.

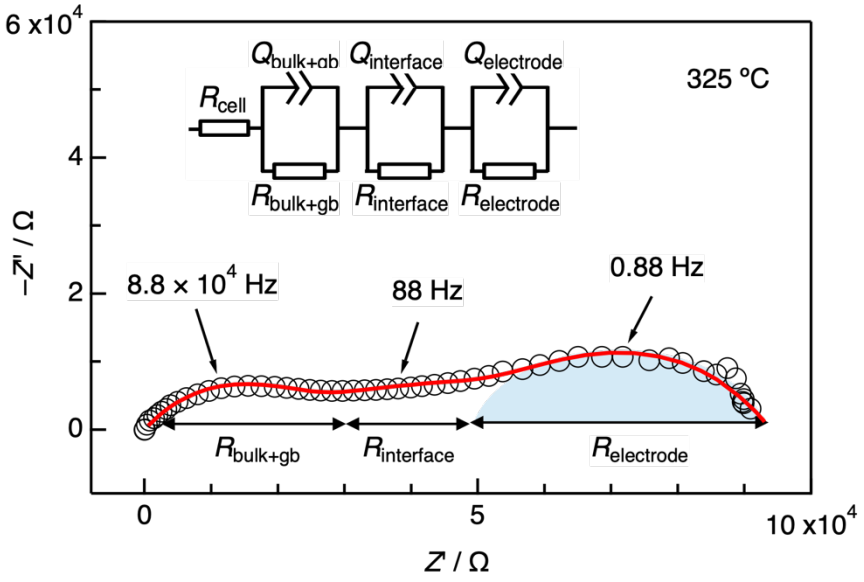

Figure 2 Impedance spectrum of a three-layered symmetric cell composed of $BaTiO_{2.5}H_{0.5}$|$LaSrLiH_2O_2$|$BaTiO_{2.5}H_{0.5}$ at 325 ºC. The Equivalent circuit used for fitting the spectrum is shown. *R* and *Q* represent resistance and constant phase element (CPE). The red solid line is the fitting result.

Secondly, $BaTiO_{3-x}H_y$ thin film was fabricated by a radio frequency magnetron sputtering method. In electrochemical devices, the reduction of total resistance is expected to more efficient electrochemical reaction. In the aforementioned study of $BaTiO_{3-x}H_x$ powder, the

electrode/electrolyte interface resistance accounted for over half of the total resistance, suggesting that there is not enough powder-to-powder contact. Thin film electrodes are expected to reduce the total resistance and the interface resistance by improving the contact with the solid electrolyte. In this study, direct sputtering with the target composed of $BaTiO_3$ and TiH_2 powders was performed. Obtained black thin film, which may be derived from Ti reduction, was fabricated by sputtering on Si (100) substrate under H_2 and Ar atmosphere. The patterns of (110)-oriented cubic-perovskite phase were detected by X-ray diffraction (Figure 3). As a result of Rutherford backscattering and hydrogen forward scattering spectrometry, the composition of the thin film was determined to be $Ba_{0.39}TiO_{1.93}H_{0.04}$. This result suggests that it was possible to directly fabricate Ba-Ti oxyhydride thin film by the target made from oxide and hydride. A symmetric cell composed of the thin film electrode and hydride ion conductor $Ba_{1.75}LiH_{2.7}O_{0.9}$ powder was evaluated by electrochemical impedance spectroscopy to evaluate hydrogen permeability under H_2 gas. In the case of $BaTiO_{3-x}H_x$ powder, the resistance derived from the conductor was not evaluated accurately due to its high resistivity of $BaTiO_{3-x}H_x$ powder. In contrast, the thin film electrode enabled us to evaluate the conductivity of hydride ion conductor $Ba_{1.75}LiH_{2.7}O_{0.9}$, which means the thin film electrode functioned as a hydrogen reversible electrode. These results confirm the superiority of the thin film electrode layer of $BaTiO_{3-x}H_y$.

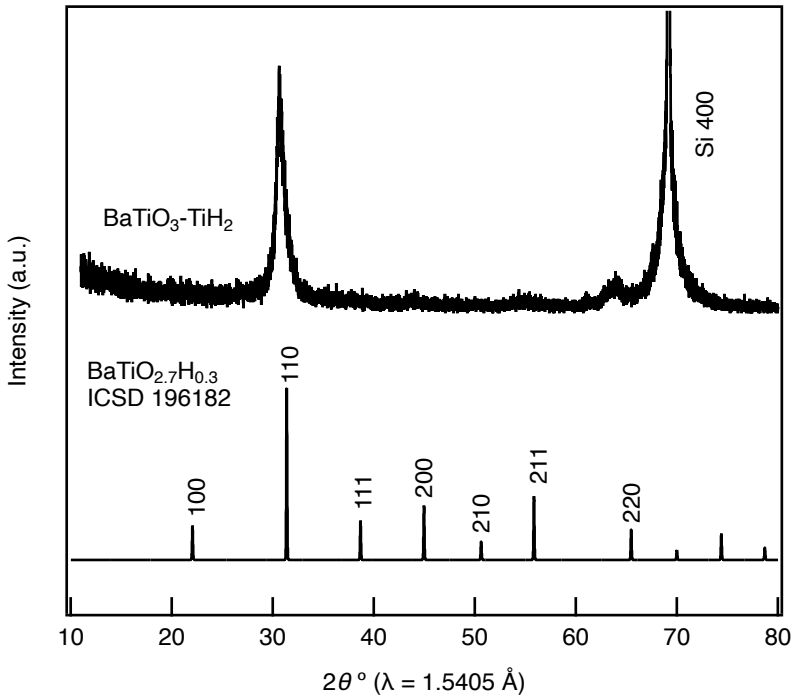

Figure 3 Laboratory XRD patterns of obtained $BaTiO_{3-x}H_y$ thin film. The bottom XRD pattern indicates $BaTiO_{2.7}H_{0.3}$ powder data obtained from the previous data (ICSD No.196182).

In this thesis, perovskite-type oxyhydride $BaTiO_{3-x}H_x$ was synthesized by the mechanochemical method and demonstrated its performance as a hydrogen-permeable electrode for the first time. Furthermore, the successful directly thinning of $BaTiO_{3-x}H_x$ and the fabrication of a symmetric cell composed of $BaTiO_{3-x}H_x$ and $Ba_{1.75}LiH_{2.7}O_{0.9}$ would be an elemental technology toward the development of electrochemical devices using H^- conductivity.

Reference

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[3] Y. Tang et al., *Adv. Energy Mater.* **8**, 1801772 (2018).

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[5] T. Uchimura et al., *J. Mater. Chem. A* **9**, 20371 (2021)