

STUDY ON HYDROGEN ISOTOPES BEHAVIOR IN PROTON CONDUCTING ZIRCONATES AND RARE EARTH OXIDES

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論 文 内 容 の 要 旨

Thesis Summary

In the high-temperature electrolysis method, proton-conducting oxides are potential materials in the hydrogen isotope separation and steam-electrolysis processes in hydrogen energy and nuclear fusion systems. In the fusion reactor fuel system, the proton-conducting oxides are used for purifying the tritium-containing exhaust gases to measure tritium concentration and to re-fuel of purified tritium. Other oxide materials such as rare-earth oxides also play an important role as a barrier material in preventing hydrogen permeation out of structural materials in the fusion reactor. Though it is important to understand hydrogen isotope behaviors especially the solubility and diffusivity of hydrogen in such oxide materials to use them as a functional material in a fusion reactor, data are limited and scattered as well. Therefore the motivation of this research is an in-depth study on the hydrogen isotopes behaviors in the oxide materials.

In the present study, as the proton-conduction oxides (PCO), zirconates were selected: the Y- and Co-doped barium zirconates, i.e., $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ (BZY), and $\text{BaZr}_{0.955}\text{Y}_{0.03}\text{Co}_{0.015}\text{O}_{2.97}$ (BZYC), and the In-doped calcium zirconate, i.e., $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{2.95}$ (CZI). As the rare-earth oxides (REOs), Y_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Dy_2O_3 , Er_2O_3 , and Yb_2O_3 were selected. In order to precisely measure the hydrogen behavior in oxide materials, two powerful techniques are adopted: Tritium tracer methods like the tritium imaging plate (TIP) technique and thermal desorption spectroscopy (TDS) method. The Tritium Migration Analysis Program, Version 4 (TMAP4) was used to compare the experimental results and understand the hydrogen behavior in the oxide materials. To clarify the proton conductivity and its isotopic effect in the oxide materials, hydrogen conductivity data of the PCOs and REOs were obtained in various gas atmospheres.

The thesis includes five chapters explaining the various experimental and simulation findings.

Chapter 1 gives an overview and importance of the two potential next-generation energy systems, i.e., nuclear fusion reactors, and hydrogen fuel cells where hydrogen or hydrogen isotopes would be used as fuel. A brief description of proton-conducting oxides, perovskite zirconate oxides is provided, which could be used as potential materials for electrochemical hydrogen devices. Finally, this chapter clarifies the motivation and objectives of the thesis.

Chapter 2 provides the experimental details of all studies, like sample preparation, characterizations, and analysis. Different types of hydrogen isotopes like HT gas, DT gas, DTO vapor, D₂ gas, and D₂O vapor were used to exposure to the samples for the TIP and TDS experiments. Conductivity measurement of the samples to examine the proton conductivity is provided. The principal of the TIP technique, TDS method, and TMAP4 simulation consideration are also briefly discussed in this chapter.

Chapter 3 presents the structural and morphological results of the sintered BZO samples. Then tritium, deuterium, and heavy water exposure results for the zirconates samples were provided to explain the hydrogen behavior such as dissolution, release and distribution, and to determine hydrogen solubility, and diffusivity properties. Hydrogen dissolution and release behavior along with the hydrogen solubility were analyzed using the TDS method. Hydrogen distribution, solubility, and diffusivity were discussed using the TIP technique. This chapter also provides the comparative conductivity results of the BZY and BZYC samples under various hydrogen atmospheres to understand the possible isotopic effect.

Chapter 4 presents the structural and morphological results of the sintered REO samples based on the TDS method and TIP technique. TMAP4 simulation results were used to discuss and verify the obtained hydrogen behavior of the REO samples obtained from TDS and TIP methods. This chapter also provides comparative conductivity results of the Gd₂O₃ sample under various hydrogen atmospheres to understand the possible isotopic effect and proton conducting properties.

In Chapter 5, the thesis ends with the major findings where the originality and contribution of the author and recommendations for future improvement have been made.

In summary, one order higher solubility and diffusivity for BZYC than BZY was found. It suggests that only a small amount of sintering-aid cobalt doping along with yttrium may play a vital role in the enhancement of the electrochemical activity of the proton conducting BaZrO₃ under HT or DTO exposure conditions. From the REO's experimental results and discussion, the REO materials were categorized into two kinds in terms of their crystal structure and hydrogen solubility: monoclinic specimens of Sm₂O₃, Eu₂O₃, and Gd₂O₃ had relatively high hydrogen solubility and diffusivity, while cubic Y₂O₃, Dy₂O₃, Er₂O₃, and Yb₂O₃ had lower ones. The REOs studies suggest that the cubic REOs could be suitable in a nuclear fusion reactor as the tritium barrier materials.